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Japan

SELECTIONS FROM FUTURE
INDUSTRIAL TECHNOLOGY SYMPOSIUM

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SCIENCE & TECHNOLOGY

JAPAN

SELECTIONS FROM FUTURE INDUSTRIAL TECHNOLOGY SYMPOSIUM

Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES,
MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88

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Foresight, Creativity Needed for R&D

43063802a Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 22-24

[Article by Shinroku Saito, professor emeritus at Tokyo Institute of Technology: "The Way R&D Should Develop in Terms of New-Material Development"]

[Excerpts] The factors to be considered first in probing the way R&D should develop are the organization and people. There are various types of organizations such as private enterprises, public concerns, universities, and international joint organizations, and they have different mechanisms. What is most important to them all in terms of R&D is to determine foresighted R&D themes. An example of a national project which achieved a great ripple effect is the U.S. Apollo Project under which NASA succeeded in landing men on the moon. The project constituted a national task of the United States for challenging the Soviet's lead in space development. The successful accomplishment of this project served to greatly stimulate subsequent space development work. Its ripple effect was extremely far-reaching. In fact, it may be attributed to the U.S. success in the Apollo Project that Japan subsequently accelerated its rocket development work for upgrading its μ rockets into N rockets and then into H rockets. After accomplishing the Apollo Project, the United States proceeded to build a space station. Thus, the United States has been producing successive stimulants to space development work. Setting aside the question of whether to recognize the SDI project as a latest development along the course of such space development work, the Apollo Project may be said to have exemplified that a country, in order to motivate its scientists to promote R&D, should play a leading role by setting a foresighted R&D theme.

The EURATOM and EUREKA programs successively inaugurated in Europe are other examples of R&D schemes to be carried out under the leadership of the countries involved. These programs have also been contributing to deepening the feeling of being united among the countries of the European Community. Japan has proposed the Human Frontier Science Program: a theme of international R&D collaboration. So far, however, this country has been slow in making progress in the program not only outwardly vis-a-vis other countries but also within itself. The author wonders if this is because this country is under the pressure of a historical shadow formed while it

confined itself to playing auxiliary roles for the promotion of U.S.-led projects. At any rate, to expedite R&D, it is important for a country to assume leadership in a foresighted manner. When a country assumes leadership for the promotion of R&D, the private enterprises, universities, and other organizations will be encouraged to orient their R&D activities in line with the national leadership

Needless to say, it is not only the national leadership that affects the orientation of private enterprises' R&D activities. In reality, most R&D targets pursued by private enterprises stem from fierce marketplace competition. In such a situation, too, it is important for the private enterprises to be farsighted. The way (Gresser) would put it, foresight is required to comprise ability to see whether research work carried out under a certain theme will lead to the introduction of a new strategic line of business. When industry is divided into three categories, i.e., basic industry, major industry, and strategic industry, it can be said that iron was identified with both basic and strategic industry. Similarly, any type of new materials can be the components of both basic and strategic industries, though the industries may vary in scale.

What the organizations as discussed above demand is the creativity of people working in them. Creativity has been discussed in academic circles and the industrial world over the last 10 years. There is no specific measure for extracting creativity from people.

Regarding the question of whether the Japanese people have creativity, there are two problems to be considered. One concerns the Japanese people's fear, which is based on their reflection, that their country may be regarded by other countries as a follower in the international arena of scientific technologies. The other is whether the Japanese people can take a unique retreat, that is, whether they can make innovations on their own in science and technology--an area which will start, or has already started, to become increasingly closed. With regard to these problems, the conclusion that the Japanese are inherently inferior to the advanced countries in the West will not convince anyone. The approach in which individual differences in everyday educational scenes are used as the basis for assessing the difference in ability between different peoples, races, or countries will also be denied. Therefore, the proper approach to be used here is to discuss, based on the premise that all individuals are generally identical in their inherent ability, what affect their ability will have in the course of their lifetime.

In the present article, prepared as a lecture text, the author has explained the necessity for the nation to be foresighted and, as a means of probing for measures to enable scientists to display their creativity, discussed obstacles to the progress of science. Nowadays, research work for the development of new materials deals with phenomena at atomic or molecular levels. In doing such research work, it is necessary to study chemical bonds in terms of such fundamental factors as ions, covalence, metallic properties, and molecularity. It is then necessary to study various intermediates from the standpoint of developing single-component materials or compound materials in the form of bulk, thin film, fiber, or

fine particles, or as porous or component-gradient materials, or from the standpoint of in-situ processing. In any case, the fundamental requirements to be met to facilitate such research work include working out foresighted projects, eliminating the factors which prevent scientists from showing creativity, and creating pliable environments in society as well as at work places and homes.

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Progress in Developing High-Stiffness, High-Strength Polymers

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[Article by Tsunesuke Doi, Research Association for Basic Polymer Technology: "Recent Progress in High Performance Plastics"]

[Excerpt] **Abstract:** Engineering plastics are a group of polymers offering high strength, stiffness, toughness, and resistance to heat, etc. They are so labeled because their structural properties allow them to replace metals in engineering applications. The five main material types dominating the marketplace are nylons, polyacetals, polycarbonate, polybutyleneterephthalate, and modified polyphenyleneoxide. From the plastics industry's point of view, there remains an enormous volume of metal applications still to aim at. Greater stiffness of plastics is an important research target. Endeavors to obtain plastics of high stiffness and strength have deep roots in the science and technology of macromolecules.

In this paper, recent progress in high performance plastics including our experimental results will be reported.

1. Progress in Engineering Plastics

Discussion in this paper is focused on polymers with high elastic moduli.

Before discussing high elastic-modulus polymers, it is necessary to touch on engineering plastics. Many people remember that the term "engineering plastics" was used first by Du Pont when the company introduced the polyoxymethylene resin about 30 years ago. This term apparently means that the engineering plastics are intended to replace metals. Materials to replace metals must meet requirements such as high strength, elastic stiffness, shock resistance, and heat resistance. The strength and resistance of polymers are roughly proportional to their elastic stiffness, so that a polymer with a high elastic modulus may be regarded as having high strength and heat resistance. However, no correlation can be found between their shock resistance and either strength or elastic stiffness. If a polymer having a high elastic modulus and high shock resistance is developed, it may be said to have a very promising future. In this

article, however, attention will be centered on the elastic moduli of polymers, setting aside their shock resistance.

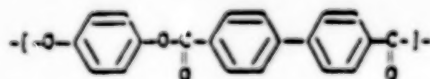
Of the five main types of engineering plastics in which polyoxymethylene and nylon are included, polycarbonate, modified polyphenyleneoxide, and polybutyleneterephthalate were developed later than polyoxymethylene. The five main types of engineering plastics do not differ much in elastic stiffness. Their elastic moduli range from 2 to 3 GPa. Engineering plastics such as polyetheretherketone [PEEK] and total aromatic polyester developed later than those mentioned in the foregoing have higher elastic moduli, which range from 4 to 10-odd GPa. Thus, engineering plastics with a double-digit elastic modulus have finally become available. However, even those higher elastic moduli which have been achieved for engineering plastics are still lower by about one order of magnitude than those of metals such as 70 GPa of aluminum and 200 GPa of steel. Even though the elastic moduli of the five main types of engineering plastics are low, their market has been expanding at an annual rate of about 15 percent in Japan and it can be said that they have been mainly replacing metals. If their elastic moduli are raised to a level equal or comparable to that of metals, what will ensue? If such engineering plastics are developed, even if they are considerably more expensive than metals, their replacement of metals will be further accelerated in various industrial fields including transportation equipment where their properties such as low specific weight and high corrosion resistance and workability will prove useful.

2. Theoretical Elastic Moduli of Polymers

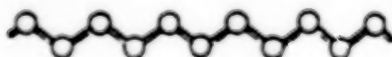
How far will it be possible to raise the elastic moduli of polymers?

The theoretical modulus of elasticity in the direction of molecular chain axis of a crystalline polymer can be calculated. To calculate the theoretical elastic modulus of a crystalline polymer, it is necessary that its structure or its cross-sectional area per molecular chain and the constants of its intermolecular and intramolecular forces be known. Among the well-known calculation methods are Treloar's method and the one invented jointly by Tashiro, Kobayashi, and Tadokoro. The theoretical elastic moduli of some polymers have been calculated using the above methods. Those with a high theoretical elastic modulus include polyarylate (4,4'-diphenyldicarboxylic acid + hydroquinone) with a theoretical elastic modulus of 154 GPa, polyethylene with 316 GPa, poly-p-phenylene-benzobisthiazole with 370 GPa, and poly-p-benzobisthiazole with 588 GPa.

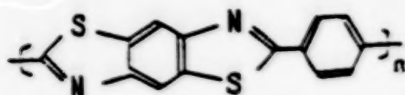
polyarylate(diphenyldicarboxylic acid + hydroquinone)



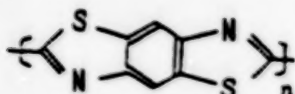
polyethylene



poly-p-phenylene benzobisthiazole



poly-p-benzobisthiazole



The calculated values are, as mentioned in the foregoing, the theoretical moduli of elasticity along their molecular chain axis. Their theoretical moduli of elasticity in the directions perpendicular to their molecular chain axis are as low as several GPa. Now that polymers with a high theoretical moduli of elasticity in the direction of their molecular chain axis are available, it is possible to produce, by molding appropriately oriented such chain polymers, polymer materials having high elastic stiffness in the direction in which they are oriented. It is also suggested that polymers, whose theoretical modulus of elasticity in the directions perpendicular to the direction in which they are oriented is low, require cross-linking for reinforcement.

What will the theoretical moduli of elasticity of three-dimensionally cross-linked polymers be like? The theoretical modulus of elasticity of the diamond has been calculated. As for other general three-dimensionally cross-linked polymers, it is extremely difficult to define regular three-dimensional structures for them. Probably for this reason, no one appears to have attempted to calculate their theoretical moduli of elasticity. It is difficult to think of synthesizing such compounds without any data on this. To provide some information relevant to the moduli of elasticity of three-dimensionally cross-linked polymers, the author discussed the relationship between the number of chemical bonds per unit area and the modulus of elasticity when this symposium was held for the third time. According to the contents of the discussion, in order to synthesize a polymer whose three-dimensional modulus of elasticity is 100 GPa or more, it is necessary to make provision for having 100 or more chemical bonds arranged in every 1,000 cubic angstroms.

3. Current State of Research Results

Finally, the current state of research work on polymers will be outlined centering on the results of our own research work.

We have been researching polymers under the Next Generation Industrial Basic Technology Research and Development System which is a 10-year program inaugurated in FY 1981 by the Agency of Industrial Science and Technology. Our aim is to develop a polymer with a high degree of crystallinity and a

modulus of bending elasticity--a typical mechanical property--of 100 GPa (10,000 kgf/mm²) or more in order to contribute toward expanding the applications of polymers in wide fields including structural materials and utilizing such features of polymers as light weight, high corrosion resistance, and suitability of diversified purposes. The polymers are broadly divided into anisotropic materials and isotropic materials. The points in our research work on anisotropic materials are how to synthesize rigid, tough, and easy-to-form chain polymers, orient them with a high degree of control, and cause as many chemical bonds as possible to be formed between molecular chains. As for isotropic materials, study is focused on how to make dense three-dimensional cross-linking. In the following, the results of our research work made for the above-mentioned program are compared with the current status of research work underway in other parts of the world. The comparison is made as to the following polymers:

(1) Anisotropic materials

- Polyarylate
- Magnetic field-oriented liquid-crystal polymers
- Molecular composite materials

(2) Isotropic materials

- Ion cross-linked polymers
- Diacetylene cross-linked polymers

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Crystals of Two-Dimensionally Cross-Linked Polymers Produced

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[Article by Hachiro Nakanishi, Research Institute for Polymers and Textiles: "Crystals of Two-Dimensionally Cross-Linked Polymers"]

[Text] **Abstract:** Multidimensionally cross-linked polymers with high crystallinity must be a better candidate of super-high performance plastics. Using the solid-state topochemical polymerization of specifically designed diacetylene monomers, we have prepared crystals of two-dimensionally cross-linked (2-D) polymers for the first time. Diacetylene-nylon salt crystals, composed of diacetylenedicarboxylic acid and diamine, gave nylon salt crystals of 1-D polydiacetylenes by γ -ray irradiation, and the nylon salt parts were thermally converted into polyamide linkages, being perpendicular to the polydiacetylene chains, to give 2-D polymer crystals. The polymer crystals had the same shape as those of the starting monomer crystals, i.e., ribbon-shaped and several microns in width, and could not be molded. However, when monomer crystals or nylon salts of polydiacetylenes were subjected to a reaction molding under high pressure of several GPa, rod-shaped specimen (2 mm ϕ x 4 mm) of 2-D polymers were obtained, and one of the specimens marked the highest Vickers' hardness of 188 ± 28 , which is far greater than 132 of iron.

1. Introduction

Considering the structure of the diamond, it may be said that designing isotropic polymers having high strength and elastic stiffness is to design the perfect crystallization of multi-dimensional covalent polymers. However, it is difficult to materialize such isotropic polymers based on the conventional method of synthesizing cross-linked polymers or that used to crystallize one-dimensional polymers with a high degree of orientation. We thought that using the technique for solid-state topochemical polymerization and that for making polymerization and crystallization simultaneously may be a good way to achieve sequence control to produce such isotropic polymers because these techniques will enable the crystal lattices of the starting monomers to be taken over as they are by the higher-order structures of the polymers to be produced. We have continued research based on the above consideration for several years.¹ In this

two-dimensionally cross-linked polymer crystals in a higher degree of perfection can be produced from DAN885 using Method I; i.e., by first producing a one-dimensional single-crystal polymer through the solid-state polymerization of diacetylene--a topochemical reaction process attainable with a high degree of perfection--then making thermal solid-state polycondensation, a process which involves large molecular fluctuations. When analyzed by the X-ray diffraction method, the products obtained by Method I showed strong diffraction peaks corresponding to the interplanar spacing of two-dimensional sheets. When microscopically observed, their shapes looked identical to those of the starting monomer crystals (shaped like ribbons measuring several μ in width).

3. Molding by High-Pressure Reaction

The two-dimensionally cross-linked polymer crystals produced were microcrystals and it was impractical to directly measure their mechanical properties. We tried to mold them by applying several tens of thousands of atmospheres of pressure, but, when the high pressure was removed, the crystals regained their bulk state in which they are fibrous crystalline aggregates. Subsequently, we tested another method in which the two-dimensional solid-state polymerization reaction process is carried out under high pressure so as to mold the polymer crystals at the same time as they are two-dimensionally cross-linked.

We put samples in teflon capsules, set the capsules in pyrophyllite together with carbon heaters, and made them undergo a thermal reaction process under up to 60,000 atmospheres of pressure in a link-type pressurization system. Diacetylene can be made to undergo solid-state polymerization just by placing it under several tens of thousands of atmospheres of pressure. Therefore, we were permitted to use not only polydiacetylenes prepared by γ -ray irradiation but also DAN monomers as the starting materials. In a pressurized state, the polycondensation reaction of nylon salts occurred at as wide a range of temperature as 150°C to 280°C, resulting in the formation of two-dimensionally cross-linked polymer crystal compacts (cylinders measuring up to 2 mm in diameter and 4 mm in length due to limitation imposed by the fixed capacity of the high-pressure container used). At a temperature of 280°C or higher, amide bonds apparently disappeared. At a temperature of 350°C or higher, carbonization reaction occurred.

4. Mechanical Properties

We measured the Vickers hardness Hv of small cylindrical samples produced under several tens of thousands of atmospheres of pressure. The Vickers hardness is a mechanical property which is positively correlated with the modulus of elasticity E and equal to three times the yield point. Among the two-dimensionally cross-linked polymers we produced, the Hv value varied from one type to another. Among the same type of compounds, those produced under a higher pressure and at a higher reaction temperature showed higher Hv values. In particular, the sample produced by molding one-dimensional polydiacetylene, which was prepared by irradiating DAN885 with γ rays, at the same time as it is two-dimensionally cross-linked under

50,000 atmospheres of pressure, recorded an Hv value of 188 ± 28 , which is higher than those of pure iron (Hv = 132, E = 206 GPa) and copper (Hv = 94, E = 123 GPa).

5. Conclusion

Polymer crystals having multidimensional covalent bonds, on which almost no research has been carried out previously, have been synthesized based on a topochemical solid-state polymerization design and part of their superior performance has been clarified. From now on, we intend to tackle the challenging task of synthesizing three-dimensionally cross-linked polymer crystals to realize soft diamond, while also continuing research work on two-dimensionally cross-linked polymer crystals to clarify more properties and study different methods of molding them.

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Ion-Crosslinking Polymer Compacts Evaluated

43063802d Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 43-45

[Article by Tetsuo Konno, Research Association for Basic Polymer Technology: "Shaped Products of Ion-Crosslinking Polymers"]

[Text] **Abstract:** In order to obtain polymer materials which are isotropically high-strength and high-modulus, it is thought that to utilize strong intermolecular interactions is effective. Then ion-crosslinking polymers composed of acid polymers and polyvalent metal ions are investigated, because an ionic interaction is much stronger than the other intermolecular interactions. As a molding method, a compression molding in powder form is used, because the strong intermolecular interaction is expected to act effectively to make adhesion of powder particles under heat and pressure. Mainly divalent and trivalent metal salts of poly(acrylic acid) are investigated. The Young's moduli of them are from 30 to 47 GPa, which are much higher than the value expected from mixtures of poly(acrylic acid) and corresponding metal oxides, and the Young's moduli are nearly proportional to equivalent of metal ions per unit volume.

1. Introduction

The Young's moduli of polymer crystal phases depend on the type and sequence of anisotropic covalent bonds, but those of noncrystal phases are dependent on relatively isotropic intermolecular forces. Therefore, to obtain polymer materials having isotropically high strength and high Young's modulus, it is necessary to make effective use of intermolecular forces. The intermolecular forces can broadly be divided into four types of interactions, i.e., van der Waals interactions, dipole-dipole interactions, electron-transfer interactions, and electrostatic interactions. The four types of interactions act mainly on nonpolar molecules, polar molecules, hydrogen-bond molecules, and ionic molecules, respectively. Of the four types, the electrostatic interactions are most strong, so that we have studied ion-crosslinking polymers composed of acid polymers cross-linked by polyvalent metal ions.

Table 1. Intermolecular Forces and Moduli

| Polymer | Main Interaction | Constants | | | Moduli | |
|----------------------|-------------------|-----------|---|-----------------------------|-------------------|-------------------|
| | | a | b | Ue (KJ/cm ³) | K (GPa) | E (GPa) |
| Poly(ethylene) | van der Waals | 12 | 6 | 0.27 | 2.2 | 2.2 ¹⁾ |
| Poly(styrene) | van der Waals | 12 | 6 | 0.36 | 2.9 | 2.9 ¹⁾ |
| Poly(vinyl chloride) | Dipole-Dipole | 12 | 6 | 0.40 | 3.2 | 3.2 ¹⁾ |
| Poly(acrylonitrile) | Dipole-Dipole | 12 | 6 | 0.68 | 4.9 | 4.9 ¹⁾ |
| Nylon 6 | Electron-Transfer | | | 0.78 | 6.3 ²⁾ | 6.3 ¹⁾ |
| Cellulose | Electron-Transfer | | | 1.02 | 8.2 ²⁾ | 8.2 ¹⁾ |
| LiCl | Electro-Static | 7 | 1 | 39.4 | 30.6 | 45.9 |
| NaCl | Electro-Static | 8 | 1 | 27.8 | 24.7 | 37.1 |
| CaCO ₃ | Electro-Static | | | | 70 | 105 ³⁾ |
| BaCO ₃ | Electro-Static | | | | 50 | 75 ³⁾ |

¹⁾ Calculated on the assumption that E=K

²⁾ Calculated on the assumption that a=12 and b=6

³⁾ Calculated on the assumption that E=1.5K

2. Experiment

We produced ion-crosslinking polymers by refining the isolated precipitates obtained by mixing different types of acid polymer solutions with metallic compound solutions. The acid polymers we used include poly(acrylic acid) (PA), poly(methacrylate) (PM), polystyrene carboxylic acid (PSC), and polystyrene sulfonic acid (PSS). The metallic ions used include zinc (Zn), calcium (Ca), and aluminum (Al) ions. We confirmed the formation of ion crosslinkage by observing infrared-ray absorption and X-ray diffraction. For thermal property assessment, we used such methods as TG/DTA [thermo-gravimetry/differential thermal analysis] and DSC [differential scanning calorimetry]. We produced sample compacts by heating sample powder at up to 250°C in a vacuum and then applying a pressure of up to 10,000 atmospheres of pressure to them. The compacts were cut and ground into test pieces. Their mechanical and thermal properties were evaluated using an autograph, a dynamic Young's modulus measuring system, and TMA.

3. Results and Discussion

3.1 Chemical Properties

When acid polymers are cross-linked by metallic ions, their thermal degradation temperature rises about 200°C and it becomes impossible to measure their glass transition temperature (T_g). The reason for this is thought to be as follows: When metallic ions are introduced into a polymer, their cohesive energy increases and the enthalpy change (ΔH_m) that occurs when it is fused becomes large relative to the entropy change (ΔS_m). As a result, the value of T_g ($T_g = (2/3) \sim (1/2) T_m$, $T_m = \Delta H_m / \Delta S_m$) estimated based on the values of ΔH_m and ΔS_m rises. In such a state, the polymer allows degradation to occur before glass transition.

Whereas the hydrophilicity of PA, PM, and PSC metal salts is small, that of PSS metal salt is large. This is assumed to be because PSS is a strong acid whereas the others are weak acids. Similarly, the hydrophilicity of acid polymers cross-linked by alkaline ions or alkaline earth metal ions is large, but that of acid polymers cross-linked by other metallic ions is small. Crosslinkage made using univalent or divalent metallic ions is stable. It is also relatively stable when made using trivalent metallic ions. However, crosslinkage made using tetravalent metallic ions is unstable so that, if an ion-crosslinking polymer formed using trivalent metallic ions is put in water, it degrades into an acid polymer and a metal oxide. This is thought to be attributable to the relatively strong covalent bonds of trivalent metallic ions.

3.2 Mechanical and Thermal Properties

The ion-crosslinking polymers have high density, strength, and Young's modulus. Of the four types of ion-crosslinking polymers, the PA metal salt has the highest Young's modulus and the PSS metal salt the lowest. This is thought to be because, among the four types of metal salts, the ion density per unit weight of the PA metal salt is the highest whereas that of the PSS metal salt is the lowest.

Table 2. Chemical Properties of Ion-Crosslinking Polymers

| (a) | Glass transition temperature (°C) | Degradation temperature (°C) | | |
|------------------------------|--------------------------------------|---------------------------------|----------------|----------|
| PA (Metal salt) | 106 (-) | 200 (400-500) | | |
| PM, PSC, PSS (Metal salt) | - (-) | 210-250 (400-500) | | |
| | | | | |
| (b) | Hydrophile property | | | |
| PA, PM, PSC metal salts | Small | | | |
| PSS metal salts | Large | | | |
| | | | | |
| (c) | Ion-crosslinking polymer | | Metal compound | |
| | Hydrophile property | Ion-crosslinking | Hydroxide | Oxide |
| Na | Large | Stable | Stable | Unstable |
| Mg, Ca, Ba | Large | Stable | Stable | Unstable |
| Zn, Pb | Small | Stable | Stable | Unstable |
| Al, Fe | Small | Stable | Metastable | Stable |
| Ti, Sn | Small | Unstable | Unstable | Stable |

We studied the molding conditions for the PA metal salts whose Young's moduli are the highest among those of the four types of metal salts. Their samples molded at higher temperatures and under higher pressures showed considerably higher Young's moduli and strength, even though the increase in density due to the higher molding temperature and pressure was slight. It appeared that their Young's modulus and strength excepting those of PA-Al₃ (the figure indicates the equivalent ratio of the metallic ions to the carboxylic acid) rise toward a maximum possible point as the molding temperature and pressure are increased. The molded samples, though being somewhat brittle, showed high strength and Young's moduli and good temperature characteristics (their linear-expansion coefficients and the temperature dependence of their Young's moduli were small).

The Young's moduli of the samples, the molding conditions for which have been analyzed, have been found to be nearly proportional to the metallic ion equivalent per unit volume. This suggests that the increase in cohesive energy of polymers caused by ion-crosslinking is mainly dependent on the metallic ions and that the Young's modulus of PA-Al₃, if molded under proper conditions, will exceed 60 GPa.

Table 3. Mechanical Properties of Ion-Crosslinking Polymers (Preliminary examination)

| Polymer ¹ | Molding condition | | | | Shaped product | | |
|----------------------|-------------------|------------------------|--------------------------|---------------|---------------------------------|-------------------------------|--------------------------------|
| | Atmo- sphere | Pres- sure (atm) | Temper- ature (°C) | Time (min) | Density (g/cm ³) | Modulus ² (GPa) | Strength ² (GPa) |
| PA metal salts | | | | | 1.71-2.49 | 27.8-32.4 | 0.29-0.47 |
| PM metal salts | Vacuum | 6,000 | 200 | 60 | 1.88-2.10 | 21.2-24.5 | 0.08-0.12 |
| PSC metal salts | | | | | 1.76-2.18 | 18.5-23.1 | 0.18-0.41 |
| PSS metal salts | | | | | 1.50-2.07 | 8.7-17.2 | 0.10-0.28 |

1. Zn salt, CaAl salt, Al salt
2. Compression mode

3.3 Comparison with Mixtures of PA and Metal Oxides

The Young's modulus values measured on the PA acid metal salt samples were compared with the corresponding values calculated for the mixtures of PA and metal oxides. The reason for having adopted the calculated values for the mixtures is that some metal oxides react with PA when they are heated. For the calculation, the following equation was used:

$$\log E = \phi_1 \log E_1 + \phi_2 \log E_2$$

where E represents Young's modulus, ϕ represents the volume fraction, 1 represents PA, and 2 represents the metal oxide. The comparison

indicates that the Young's moduli of the PA metal salts are about three times those of the corresponding mixtures of PA and metal oxides. The results are identical even if equations other than the above-shown are used. Also, the PA metal salts are higher in density than the mixtures of PA and metal oxides. These results are thought to indicate that the increases in cohesive energy of the sample polymers caused by the introduction of metallic ions into them resulted in their tight structures and high Young's moduli.

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20109/9365

Recent Progress in Synthetic Metals Reported

43063802e Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 47-49

[Article by Tsunesuke Doi, Research Association for Basic Polymer Technology: "Recent Progress in Synthetic Metals"]

[Excerpts] **Abstract:** It was a breakthrough when Shirakawa-Ikeda found in 1974 that acetylene was polymerized to give a freestanding film and when, a little later, MacDiarmid, et al., showed that polyacetylene becomes conductive by exposing it to oxidizing agents like iodine or arsenpentafluoride. Since then the astounding advances in the field of synthetic metals have been found. A doped polyacetylene with a conductivity greater than 10^5 S/cm was reported and a charge transfer organic complex with a superconductive transition temperature of 10 K was reported in 1987.

In this paper, recent progress in synthetic metals including our experimental results will be reported.

1. Introduction

It used to be generally considered that organic materials do not easily conduct electricity. However, it was found in 1954 that there are semiconductive polycyclic aromatic hydrocarbon compounds. Since then, research on organic semiconductors has been actively conducted. In 1974, a process for polymerizing acetylene directly into a film was developed. In 1979, it came to be known that the film produced from acetylene can be made highly conductive by doping. Furthermore, in 1979, it was discovered that the polypyrrole produced from pyrrole by the electrolytic oxidative polymerization method shows high conductivity. These developments gave impetus to R&D work on conductive polymers, or more broadly, nonmetallic materials comparable to metals in conductivity, i.e., synthetic metals. At present, both fundamental studies and research for application and development are being actively promoted. From the viewpoint of high conductivity, superconductors, which are ultimate high-conductivity materials, should be included in the synthetic metals. This paper deals mainly with conductive polymers and organic conductors (charge-transfer complexes) among the synthetic metals.

2. Conductive Polymers

The electric conductivity of a material is determined by the number of its electric charges and their mobility. In metals, their free electrons serve as electric charges. In conductive polymers, the π -electrons of conjugated double bonds formed by charge transfers caused by doping play the role of electric charges. Both metals and conductive polymers have metallic luster and are highly conductive. One of the notable differences between them is that the electric conductivity of conductive polymers is anisotropic; that is, chain polymers show high conductivity in the direction of their orientation, but their conductivity in the directions perpendicular to the direction of their orientation is low. This phenomenon has important significance. For, with the lengths of chain polymers being limited, they cannot pass electric current by means of intramolecular electric charge transfers along. In order to be conductive, it is necessary that intermolecular charge transfers take place in them. However, when they are anisotropic, intermolecular charge transfers are assumed to be more difficult than intramolecular charge transfers.

In considering the electric conductivity of conductive polymers, which are anisotropic, it is necessary to be always conscious of both intramolecular and intermolecular conductivity.

As a result of the research work done so far, it has been concluded that a soliton ranges over about 14 carbon atoms and that it moves with considerable ease. This conclusion has made it quite easy to interpret the charge solitons caused by charge transfers between dopants and molecular chains and the metallic conductivity dependent on polarons. It is assumed that, as doping of polyacetylene progresses, its electric conductivity rapidly rises and the bond alternation in it gradually disappears. In reality, however, research work on polyacetylene doped to a high concentration has not made much headway. The results of calculations of the electron state of polyacetylene have shown that the ionization potential (I_p) of polyacetylene is small, that the band width (BW) is wide, and that its band gap (E_g) is narrow. Such an electron state of polyacetylene constitutes a condition for enabling polyacetylene to be made highly conductive by doping. The values of I_p , BW, and E_g of other conjugated-system polymers than polyacetylene, such as poly(phenylene vinylene), polypyrrole, polyacene, graphite, and some other later-developed ones have been determined by electron-state calculations made by the molecular orbital method. These values can be used as reliable data based on whether the corresponding polymers can be made conductive.

Regrettably, however, we cannot but say that it is still extremely difficult to quantitatively predict the intramolecular conductivity of polyacetylene. Several years ago, it was figured among some physicists that the intramolecular conductivity of polyacetylene would be in the range of 10^4 S/cm to 10^6 S/cm. At present, it is estimated to range even up to 10^8 S/cm which is much higher than that of copper or silver.

What about the intramolecular conductivity of polyacetylene? This subject has only recently been approached theoretically and is yet to be clarified.

3. Charge-Transfer Complexes

Regarding the polycyclic aromatic hydrocarbon semiconductors mentioned in the beginning of this article, charge-transfer organic complexes, for example, TCNQ (tetracyanoquinodimethane) salt, which show metallic conductivity started being synthesized in the 1970's. The charge-transfer organic complexes so far synthesized include one which shows a conductivity of 10^3 S/cm at room temperature. Then, with the advent of the 1980's, charge-transfer organic complexes whose superconductive transition temperatures are between 0 and 11 K came to be synthesized one after another. Research work on the mechanism of electric conduction has also been actively carried out.

4. Current State of Research Results

Finally, the current state of research work on synthetic metals will be outlined centering on the results of our own research work.

We have been researching synthetic metals under the Next General Industrial Basic Technology Research and Development System which is a 10-year program inaugurated in FY 1981 by the Agency of Industrial Science and Technology. Our aim is to develop polymer materials which can be put to practical use, having a high conductivity (10^3 S/cm or more at room temperature), a stable structure, and high workability, and synthetic conductive materials which have new functions not offered by metals and can be used as electronic and electric materials. The concrete targets of our research work include the synthesis of new and existing conductive polymers, research for the development of an improved synthesis method for producing polymers with higher conductivity, studies on the moldability of conductive polymers, and clarification of the mechanism of electric condition in polymers. In the following, the results of our research work so far in this area are compared with the current states of the corresponding research being done in other parts of the world. The comparison is made as to the following polymers:

(1) Conductive polymers

- Polyacetylene
- Poly(phenylene vinylene)
- Polypyrrole
- Polythiophene
- Polyacene
- Graphite

(2) Charge-transfer complexes

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Recent Progress in Organic Conductors Studied

43063802f Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 52-54

[Article by Hiroo Inokuchi, Institute for Molecular Science: "Recent Progress in Organic Conductors"]

[Text] **Abstract:** Since the establishment of the organic semiconductor/conductor research field, many types of organic conducting materials have been found. Such materials can be classified into specific research subjects according to the value of their electrical conductivity; i.e., insulators, poor insulators, organic semiconductors, organic conductors, and organic superconductors. In this report, we wish to discuss recent developments in the field of organic conductors, and, in particular, our research into the construction of novel single component systems such as the quasi-covalent-type organic conductors.

(1) Introduction: Organic Materials Assessed in Terms of Electric Conductivity

Of diversified material properties, electric conductivity is among the most useful. This is attributable to, among other things, the wide conductivity range over which the materials used by human beings are distributed. Their conductivity extends over a 24-digit range, i.e., from 10^{-10} Ωcm to 10^{14} Ωcm . Regarding this number of digits, it is comparable to the Avogadro constant. This wide conductivity range is the basis of the interest which can be found in measuring the electric properties of materials. Figure 1 shows how widely different materials range in conductivity. In this paper, the organic materials indicated in Figure 1 will be discussed in terms of their electric properties. In this context, an outline can be itemized as follows:

(1) The feature to be mentioned first is their ability to insulate electricity. PVC [polyvinyl chloride] and polyethylene are representative of the organic materials used as insulators.

(2) Of the organic materials, those which are poor insulators also deserve attention. This group of organic materials tends to be treated lightly, but they make up a field which will continue to develop. However, I

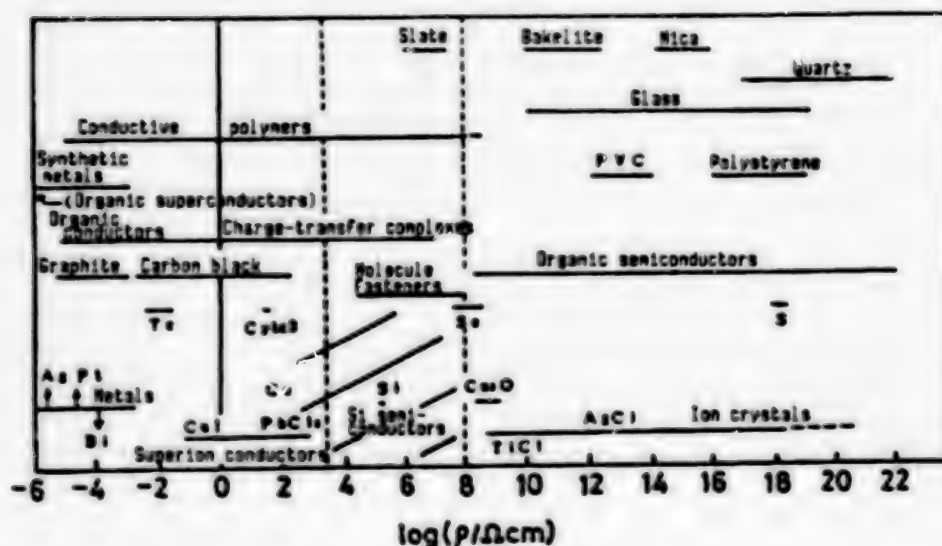


Figure 1. Conductivity of Different Materials

refrain from further discussing them here, as they fall outside the present topic of discussion.

(3) In the 24-digit conductivity range of materials, there is a "shady zone," as shown by hatching in Figure 1. The number of single-component materials falling into this zone is very small. Materials such as Si ($10^8 \Omega\text{cm}$) and Ge ($10^1 \Omega\text{cm}$) whose conductivity falls into the zone can be called special examples. Both Si and Ge are among the major electronic materials. (However, what makes them useful are their extrinsic properties rather than intrinsic ones.) Development of materials whose conductivity falls in the above zone may be an appropriate research target. In the field of organic materials, too, those whose conductivity falls in the zone were not found until 1984. I feel that the path to develop such organic materials was opened somewhat wider in and after 1984. This will be discussed in the next section.

(4) It may be said that the charge-transfer complexes still constitute the mainstream of the organic conductors. The synthetic metals come on the line extended along the development of charge-transfer complexes. The organic superconductors first developed in 1980 come on where the same line is further extended. I think that these types of organic conductors can be the best subjects when reviewing the recent progress in organic conductor development.

(5) In Japan, research on conductive polymers is being conducted quite systematically. The researchers working in this field in Japan are probably the most advanced group of conductive polymer researchers in the world. I leave further discussion in this regard to Chairman Doi's lecture titled "Recent Progress in Synthetic Metals."

(II) Conductive Single-Component Materials: Potential of Quasi-Covalent Organic Materials

An organic material is formed by combining independent molecules. In the process in which independent molecules are put together, covalent bonds are formed through cross-linking, thereby causing the resultant molecule collection to gain enhanced electron mobility. This is how a conductive organic material can be produced. Figure 2 shows how TTeC₁TTF molecules are combined into a crystal. The crystal, in which weak covalent bonds have been formed, shows conductivity of $10^4 \Omega\text{cm}$ which may even be abnormally high for a single-component organic material. This conductivity falls in the shaded zone in Figure 1 and the material can be regarded as an organic conductor in the broad sense. This material may be regarded as having the potential for further development.

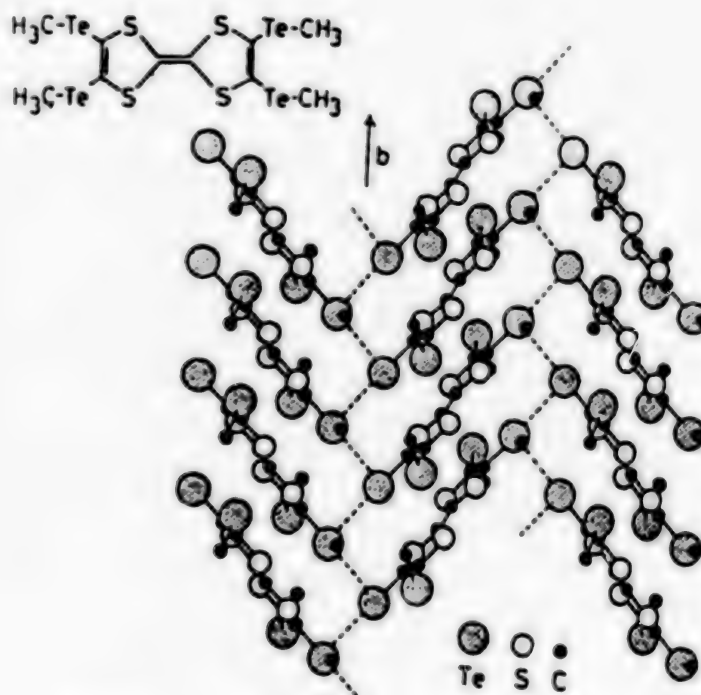


Figure 2. TTeC₁TTF Crystallization

(III) Organic Conductors Developed as Synthetic Metals

An attraction of organic conductor research is that all the developments in the field stem from the introduction of new materials. When the history of progress in the field of organic conductors, extending from the finding in 1954 that charge-transfer complexes can conduct electricity to the discovery of superconductors, is outlined in a table, it indicates that every major research development in this field was triggered by the introduction of a new material. This aspect of organic conductor development may be an attraction for chemists.

The fundamental factors affecting the formation of organic conductors include ionization energy, electron affinity, and molecule shapes. It is not always possible to clearly define these factors. In this sense, too, I wish to stress, there is room where the services of chemists are called for.

Table 1. Chronology of Organic-Conductor Development

| | |
|------|---|
| 1954 | Perylene bromine |
| 1960 | TCNQ complex |
| 1970 | TTF compound |
| 1973 | TTF-TCNQ (Synthetic metal) |
| 1980 | (TMTSF) ₂ PF ₆ (Organic superconductor) |
| 1982 | (BEDT-TTF) complex (two-dimensionality) |

(IV) Organic Superconductors

Organic superconductors have been discussed in a number of reports. I will, therefore, only briefly outline the present state of research work on organic superconductors, to encourage preparation for further research work. Superconductive transition temperatures (T_c) exceeding 10 K have already been achieved. To be sure, for researchers studying organic superconductors, achieving higher values of T_c can be a research target. I, however, wish to stress that more importance should be attached to developing new types of materials.

(V) Towards New Fields

The most important subject to be tackled by researchers engaged in fundamental research on materials is "development of new types of conductivity." It is by no means easy to accomplish the goal, but some of the possibilities in this area have already started to yield results. They include the following:

(1) DCNQI (dicyano-quinone dimine) group

Research work on this group of materials was initiated by a German researcher. They have a structure as shown in Figure 3, and regarding properties, they may be positioned between polymers and charge-transfer complexes. Research work has made new progress.

(2) Biomaterials

Biomaterials are difficult subjects to research, but material researchers should keep an eye on this field.

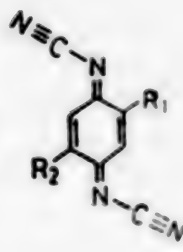
| | R ₁ | R ₂ | |
|-----------|-------------------|-------------------|---|
| DMDCNQI | CH ₃ | CH ₃ |  |
| DMODCNQI | CH ₃ O | CH ₃ O | |
| MeBrDCNQI | CH ₃ | Br | |
| DBrDCNQI | Br | Br | |
| MeClDCNQI | CH ₃ | Cl | |
| DClDCNQI | Cl | Cl | |

Figure 3. Structure of "DCNQI" Group

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BEDT-TTF Trihalide Crystals Analyzed

43063802g Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 55-57

[Article by Horiyuki Anzai, Electrotechnical Laboratory: "Properties and Crystal Structures of BEDT-TTF With Trihalides"]

[Text] **Abstract:** It is very important to investigate the relationship between crystal structures and electrical properties of organic conductors in order to materialize the designing of organic conductors. For that purpose, we have studied several crystals of (BEDT-TTF)₂-trihalide. Bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) is comparatively stable among organic donors and forms a number of charge-transfer complexes, even with the same stoichiometric formula. Several kinds of linear trihalide anions are obtained by combination of halogen atoms (I, Br, and Cl), and that they are chemically similar to each other. Therefore, crystals of (BEDT-TTF)₂-trihalide offer suitable and convenient examples for our purpose. In this talk, I will present the crystal growth, crystal structure, and properties of (BEDT-TTF)₂-trihalide based on our results.

1. Introduction

It is estimated that there are about 3 million types of organic conductors ranging widely from insulators to superconductors. Research work on organic conductors is important for the progress of organic solid physics and for developing the applications of such materials. So far, several hundred types of organic conductors have been synthesized. In the process of developing a new organic conductor, material design assumes great importance. To design an organic conductor, it is important to study the relationship between the crystal structures and electrical properties of organic conductors. Among the organic donors, BEDT-TTF is relatively stable. In addition, its complexes, while being stoichiometrically identical, can assume different crystal structures. Various types of linear trihalide anions obtained from combinations of halogen atoms (I, Br, and Cl) are chemically alike. We thought that complex crystals of BEDT-TTF and trihalide anions can be used as very suitable models in our study of the structures and properties of organic conductors. Based on this, we have been studying BEDT-TTF trihalide complex crystals.

On this occasion, I will talk about the growth of BEDT-TTF trihalide complex crystals, the crystal structures, and the electrical properties of the crystals.

2. Crystal Growth

As the starting material, we used commercially obtained BEDT-TTF after refining it. To synthesize the tetrabutyl ammonium trihalide to be used as the supporting electrolyte, tetrabutyl ammonium halide was made to react with halogen. The organic solvent obtained was refined by distillation after being chemically processed.

To grow BEDT-TTF trihalide crystal, BEDT-TTF was electrolytically oxidized in the organic solvent in the presence of the supporting electrolyte. In one experiment, for example, 0.13 mmol of BEDT-TTF and 0.52 mmol of tetrabutyl ammonium trihalide as the supporting electrolyte were dissolved in about 60 ml of organic solvent and a constant current of 1 to 5 μ A was made to flow through the solution in a nitrogen gas atmosphere at 20°C to grow crystal. The crystal-growth period was 1 to 1.5 months.

3. Crystal Structures

The known crystal structures of BEDT-TTF trihalide include α , α' , β , β' , γ' , δ , θ , and . I will discuss the electric properties of the α , α' , β , and β' type crystals which have the same composition. Of the composition of $(\text{BEDT-TTF})_2\text{X}$, the α -type and β -type structures are known with $\text{X} = \text{I}_3$ and $\text{X} = \text{I}_2\text{Br}$; the α' -type and β' -type structures are known with $\text{X} = \text{IBr}_2$; the α' -type and β' -type structures are known with $\text{X} = \text{IBrCl}$, and the β' -type structure is known with $\text{X} = \text{ICl}_2$. The α' -type and β' -type structures resemble the α -type and β -type structures, respectively.

4. Electric Properties

$\text{Tf} \alpha-(\text{BEDT-TTF})_2\text{I}_3$ (abbreviated $\alpha\text{-I}_3$) shows metallic properties in the temperature range between room temperature and 135 K. At lower temperatures, it becomes like a semiconductor.

On the other hand, $\beta\text{-I}_3$ remains like a metal even at low temperatures. Under ordinary pressure, it is a superconductor with its transition temperature T_c coming between 1.1 and 1.5 K (low T_c state referred to as "L- T_c "). Under a pressure of 1.3 kbar, it becomes a different type of superconductor with a T_c of 8 K (high T_c state referred to as "H- T_c "). It has been clarified by observing the effects of the magnetic fields associated with the electric resistances of their samples that, once they are pressurized at a temperature not higher than 120 K, they partly remain superconductive with a T_c of 8 K even under ordinary pressure. It has been clarified by making diffuse scattering using X-rays and by analyzing the temperature dependence of the electric-resistance temperature differential that the material is converted into the two types of superconductor through a phase transition which takes place involving superlattices. The phase transition is inhibited under a pressure of 0.5 kbar or more. From the

values of H_{c2} and T_c of the β - I_3 superconductor, it has been made known that the superconductor assumes a single state. Furthermore, from the anisotropy of H_{c2} , its anisotropy at the GL coherence length has been determined as follows:

$$\xi_a(0) : \xi_b(0) : \xi_c^*(0) = 21:20:1$$

The α' - IBr_2 behaves like a semiconductor. The β - IBr_2 is like a metal. Under ordinary pressure, it transforms into a superconductor at 2.3 K, but no superlattice has been observed in it. Since the lattice constant of the β - IBr_2 is smaller than that of β - I_3 , the superconducting state of the β - IBr_2 with a T_c of 2.3 K is assumed to correspond to the H- T_c state under a pressure of 4-5 kbar of the β - I_3 .

The β - I_2Br is like a metal, but no superconducting state has been observed to occur in it. With its lattice constant being smaller than that of the β - I_3 , it is considered to structurally correspond to the H- T_c state under a pressure of 2 kbar of the β - I_3 . So far, it has not been observed to become superconductive at temperatures down to 50 mK. This is thought to be attributable to the asymmetric structure, I-I-Br, of the I_2Br anions.

The β' - ICl_2 has a structure resembling the β structure, but it is a semiconductor. The α' - $IBrCl$ is, of course, a semiconductor.

5. Conclusion

The results of our experiments, though made only with a limited number of materials synthesized from linear trihalide anions and BEDT-TTF, clearly indicate that the crystal structures of materials and their properties are closely associated. We should continue this research work on a larger variety of materials.

20109/9365

High-Conductivity, Stable Poly(Arylenevinylenes) Prepared

43063902h Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 58-60

[Article by Toshihiro Ohnishi, the Research Association for Basic Polymer Technology: "Highly Electroconducting Poly(Arylenevinylenes) Prepared via Soluble Precursor Process"]

[Text] **Abstract:** Highly conducting polymers with excellent processability and stability have been attractive from the industrial point of view since the discovery of the conducting doped polyacetylene. We have successfully prepared highly conducting and stable poly(arylenevinylenes), PAV, in film form via pyrolysis of soluble or processable precursor polymers. Highly oriented poly(p-phenylene vinylene), PPV, film obtained by stretching a precursor film showed extremely high conductivity over 5×10^3 S/cm by doping. Substitution of an alkoxy group at the phenylene ring results in the enhancement of the conductivity and stability of PPV. Poly(2,5-thienylene vinylene), PTV, film was prepared via pyrolysis of a stable and soluble precursor polymer derived from 2,5-thienylene bis(methylene dimethyl sulfonium bromide). Highly conducting graphite films also have been obtained by pyrolysis of PPV and polyimide films.

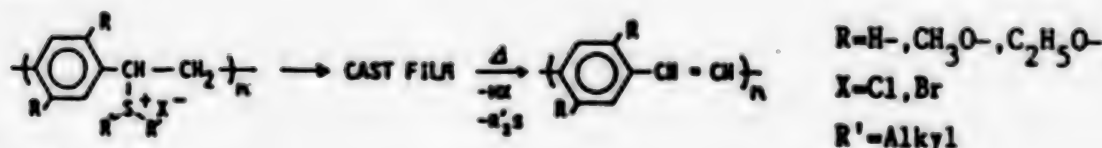
1. Development of Conductive Polymers

The discovery, made when a tendency to promote the development of new materials was growing stronger in that industry, of the metallic conductivity of doped polyacetylene has gained attention as a breakthrough which corrects the common idea that the polymers are either insulators or semiconductors. The discovery served to activate research on conductive polymers worldwide. The research work since then has made much progress in many aspects and, today, polyacetylene with a conductivity higher than that of metals can be obtained.¹ However, many of the conductive polymers so far reported to have been developed are insoluble and infusible due to the rigidity of their molecules. Therefore, its formability is low and this has limited its industrial applications.

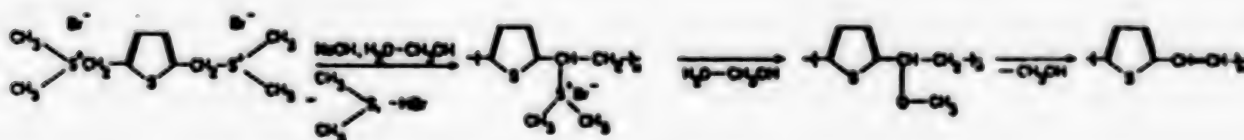
With the aim of developing a polymer material which, while excelling in formability and stability, has electric conductivity comparable to that of metal, we conducted research work by selecting poly(arylenevinylene) (PAV)

as the research object. Eventually, we succeeded in establishing a poly(arylenevinylene) synthesis process in which a soluble precursor is used and achieving conductivity of 10^3 S/cm or more with poly(p-phenylene vinylene) (PPV) and poly(thienylene vinylene) (PTV).^{2,3} We also have the possibility that the introduction of an appropriate substituent or hetero aromatic ring will make it possible to enhance the stability of these high-conductivity polymers. Furthermore, we discovered that highly conductive graphite films can be obtained by pyrolyzing PPV.⁴ In the following, the conductivity and stability enhancement achieved for PAV will be discussed:

Scheme 1



Scheme 2



2. High-Conductivity Poly(p-Phenylene Vinylene)

We have discovered that uniaxially stretching the soluble precursor for PPV film production at a temperature in the range of 100 to 400°C results in raising the conductivity of the PPV film from 40 S/cm to about as high as 5,000 S/cm and increasing its conductivity anisotropy by 100 times, as shown in Figure 1. The high conductivity and anisotropy are thought to be attributable to the uniaxial orientation of the molecules of the PPV. In particular, the anisotropy of its conductivity is a characteristic not shown by metals. From the viewpoint of intermolecular conduction, PPV is estimated to be less conductive than polyacetylene. The fact that it showed conductivity close to that of polyacetylene seems to suggest that the conductivity of these materials is dependent more on the carrier conduction between molecular chains than on that inside molecular chains.

3. Substituted Poly(p-Phenylene Vinylene)

A feature of PPV is that, with its molecules containing aromatic rings, it permits chemical modification with ease; for example, a substituent can be easily entered in its 2,5 position. To clarify the effect of a substituent on the conductivity of PPV, we substituted an electron-releasing methoxyl group for the phenylene group. As a result, we found that, as indicated in Table 1, the substituted PPV can be made highly conductive even with dopants such as iodine whose electron affinity is relatively weak. The results of molecular orbital calculations we made indicated that the substitution of the methoxyl group caused the ionization potential (Ip) of PPV to drop. From this, we have concluded that the high conductivity of the methoxyl-substituted PPV doped with iodine is attributable to the fact

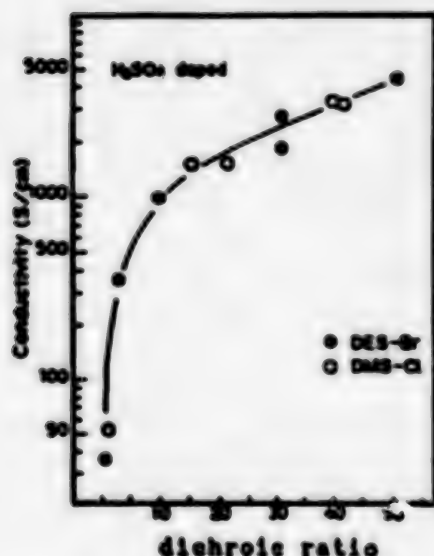


Figure 1. Relation Between Conductivity and Dielectric Ratio at $1,520\text{ cm}^{-1}$ of i.r. Spectrum of Stretched PPV

Table 1. Electrical Conductivity of Nonstretched PPV Films Doped With I_2 , SO_3 , AsF_3 , and H_2SO_4

| Substituted PPV | I_2 | | Conductivity (S/cm) | | SO_3 | | AsF_3 | | H_2SO_4 | |
|------------------------------------|----------------------|--------|---------------------|--------|---------------|-----|----------------|-----|-------------------------|--|
| | | | | | | | | | | |
| $\text{CH}_3\text{O-PPV}$ | 203 | (1.85) | 159 | (2.00) | 68 | (-) | 411 | (-) | | |
| $\text{C}_2\text{H}_5\text{O-PPV}$ | 257 | (1.17) | 43 | (0.80) | 14 | (-) | -- | | | |
| H-PPV | 2.5×10^{-3} | (0.1) | 7.7 | (0.41) | 38 | (-) | 27 | (-) | | |

that the lowered I_p enabled electron mobility high enough for carrier generation to be obtained even with dopants with weak electron affinity.

4. High-Conductivity Poly(2,5-Thienylene Vinylene)

For PPV, a stable precursor polymer containing sulfonium-salt side chains was obtained. In the case of PTV, we observed that, when alcohol is used as a polymer solvent, the alcohol is substituted for the sulfonium salt and that, as a result, a soluble precursor whose side chains contain an alkoxy group is formed. The structure of the precursor was confirmed by measuring IR, ^{13}C -, and H-NMR. This precursor is highly stable. It can be formed into a film and can be stretched. We have discovered that, when the precursor is thermally treated, the alkoxy group contained in its side chains is removed to cause a 2,5-thienylene vinylene structure to be formed. The PTV film produced has metallic luster and is quite stable in the atmosphere. The unstretched PTV doped with iodine showed a

conductivity of 200-400 S/cm. When the PTV was uniaxially stretched, its conductivity greatly increased. The maximum conductivity recorded was 2.7×10^3 S/cm. The conductivity anisotropy of stretched PTV was up to 35 times that of unstretched PTV. The deflected infrared absorption spectrum observed on stretched PTV showed a high degree of dichroism indicating that the molecules of the PTV were oriented in the direction of stretching.

5. Graphite Film Obtained Through Polymer Pyrolysis

We have discovered that a highly oriented and conductive graphite film can be obtained with ease by pyrolyzing biaxially-stretched PPV at 3,000°C. PPV retained its film form without fusing through the pyrolysis process at 3,000°C. We also learned that a graphite film produced by pyrolyzing a PPV film which has been biaxially stretched to a higher degree shows a higher conductivity. In fact, the conductivity of the graphite films we produced ranged up to 10^4 S/cm or even 10^5 S/cm (with HNO_3 intercalated), comparable to that of highly oriented pyrolyzed graphite (HOPG). X-ray diffraction photos of the biaxially stretched PPV films indicate that the films have been plane-oriented. It is assumed that their orientation structure favorably affects their graphitization through pyrolysis. As for other heat-resistant aromatic polymers than PPV, it has been found that only the aromatic polyimide can give high-conductivity graphite films.

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FRP, FRM Development Program Overview

430639021 Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 61-63

[Article by Yoshio Minoda, Research and Development Institute of Metals and Composites for Future Industries: "Introduction"]

[Text] **Abstract:** The program aims to develop high temperature structural composite materials to be used on future aerospace or surface vehicles and energy equipment.

Functional organization of the joint R&D program is as shown in Figure 1. In the following sessions, typical results to date will be presented by a representative of the technical committee covering each sub-scheme. Details will be presented in the poster session, too. We expect that the fruits of the program, including patents and computer programs, would be utilized by any industries or researchers outside of the team as much as possible.

(1) Purposes of Research

This program is an 8-year program inaugurated in FY 1981 for the purpose of developing "fiber-resin composite materials (FRP: fiber-reinforced plastics) or fiber metal composite materials (FRM: fiber-reinforced metal) which are light and have strength, rigidity, and heat resistance high enough for intended uses" as a step toward establishing the fundamental technologies for the industries expected to grow in the 1990's. The program assumes that the future composite-material applications will include large space structures, aircraft structures, turbine engines, and automobile structures. Based on this assumption, the research work made in this program is aimed at developing structural heat resistant composite materials containing fibers, mainly those produced in Japan, as reinforcers and their applications. The aims of the program also include promoting the positive utilization of the directionality of the specific rigidity and strength of composite materials and enhancing the parts' productivity and reliability through the adoption of one-part structures. In this program, the research work has been integrated to thoroughly cover "design, material development, molding, and quality evaluation."

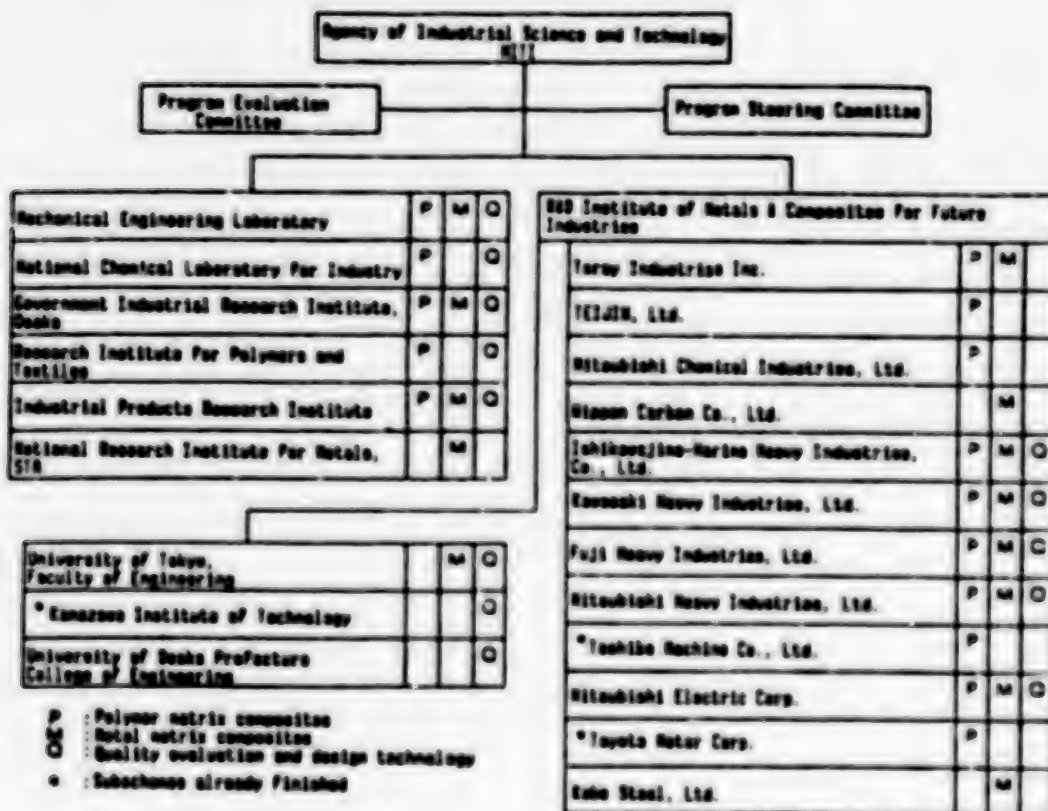


Figure 1. Functional Organization of the Joint ACM R&D Team

(2) Research Organization

The participants in this program include, as shown in Figure 1, six national laboratories and the three universities and 12 enterprises to which this institute has entrusted research in accordance with the integrated research schedule prepared for the program. Thus, this program features a research system in which the industrial, public, and academic sectors are to join forces.

(3) Research Result Utilization

In today's session, as for the research entrusted to the universities and enterprises, the results so far obtained of the work to develop high-performance FRM and FRP techniques for molding them will be reported in a limited amount of time by representatives of the technical committee of this institute on behalf of the researchers directly engaged in this work. For detailed information on the research, readers are referred to the poster session.

The results of research on the techniques for material design and quality evaluation will also be reported today, but further research is underway at universities, national laboratories, and the enterprises to which the prime contractors subcontracted work assigned by this institute. The research

targets pursued by those organizations include developing programs for laminated-structure optimization taking into account many conditions such as material rigidity, strength, and vibrations; programs for analyzing various composite structures; techniques for conducting nondestructive tests; apparatus for testing materials in simulated space environments; and composite-material databases.

In principle, the results achieved in this research program are to be made public. In line with this principle, the researchers working for this program will take the opportunity--for example, next-generation industrial technology symposiums and lecture meetings of both domestic and foreign academic circles--to directly report their achievements in detail. Or they may contribute their research reports to academic journals.

As for the industrial property rights (110 patents and 3 designs of practical utility have been obtained or applied for, as listed in Table 1, from the fruits of the research entrusted to the participants in the program) belonging to the government, the computer programs (listed in Table 2) developed in this program, and the software for composite production or processing procedures that has also been developed in this program and can be the objects of licensing: it is hoped that they will be made available to interested parties at proper prices through the Japan Industrial Technology Promotion Association.

Table 1. List of Patents (Products of assigned research)

| | | | |
|----|----|-------------|---|
| 1 | PT | 1268401 | Laser beam machining system |
| 2 | PT | 1278423 | New method of heat resistant curing resin production |
| 3 | PT | 1278424 | New method of heat resistant curing resin production |
| 4 | PT | 1359433 | Automatic FRP tape cutting device |
| 5 | PT | 1365267 | New imide compound |
| 6 | PT | 1405594 | New polyepoxy compound |
| 7 | PT | 1405594 | New polyepoxy compound |
| 8 | PB | 1987-20206 | New polyglycidyl ether, and production method |
| 9 | PB | 1987-22988 | New polyglycidyl ether, and production method |
| 10 | PB | 1987-35371 | Polymer-matrix composite material molding method |
| 11 | PP | 1984-64322 | Automatic method and device for FRP tape pasting |
| 12 | PP | 1984-166530 | Method of producing aromatic imide polymer or amidoimide polymer containing epoxy end group |

(continued)

[Continuation of Table 1]

| | | | |
|----|----|-------------|--|
| 13 | PP | 1984-166531 | Composition of curing resin |
| 14 | PP | 1984-167569 | Imido oligomer production method |
| 15 | PP | 1985-26023 | Composition of curing resin |
| 16 | PP | 1985-32821 | Composition of curing resin |
| 17 | PP | 1986-34167 | Method of producing preform wire, preform sheet, or tape for FRM, and ultrasonic vibration device for the method |
| 18 | PP | 1986-46211 | Short fiber arrangement method for the production of short fiber arranged preregs |
| 19 | PP | 1985-58551 | Device for curing-reaction voltage detection on polymer-matrix composite structures |
| 20 | PP | 1985-199018 | Epoxy resin production method |
| 21 | PP | 1985-199022 | Composition of epoxy resin for carbon fiber reinforcement |
| 22 | PP | 1985-199023 | Composition of epoxy resin for carbon fiber reinforcement |
| 23 | PP | 1985-206830 | Highly heat resistant polyquinoxaline-based copolymer |
| 24 | PP | 1985-206831 | Polyphenylquinoxaline resin prepolymer |
| 25 | PP | 1985-206836 | Method of hardness inspection during thermo-setting resin curing process |
| 26 | PP | 1985-206840 | Highly heat resistant carbon fiber-reinforced composite |
| 27 | PP | 1985-208329 | High moldability polyphenylquinoxaline resin |
| 28 | PP | 1985-210751 | Device for measuring viscosity and electrical properties of materials |
| 29 | PP | 1985-220714 | System for molding by drawing |
| 30 | PP | 1985-220715 | Continuous molding method for carbon fiber reinforced plastic cylinder production |
| 31 | PP | 1985-223825 | Prepolymer for fiber reinforced composites |

[continued]

[Continuation of Table 1]

| | | | |
|----|----|-------------|--|
| 32 | PP | 1985-223828 | Method of curing-reaction progress detection during thermosetting resin curing process |
| 33 | PP | 1985-224046 | Electrode device for curing-reaction detection on polymer-matrix composite structures |
| 34 | PP | 1985-224052 | Method of gelation time measurement on thermosetting resin |
| 35 | PP | 1985-245625 | Fiber reinforced composites and hardened moldings produced from them |
| 36 | PP | 1985-250030 | Oligoimide composition |
| 37 | PP | 1985-252251 | Resin degradation inspection method |
| 38 | PP | 1985-260624 | High moldability polyimide prepolymer |
| 39 | PP | 1985-260625 | Polyimide resin production method |
| 40 | PP | 1986-19338 | Method and device for preventing tape separation in automatic FRP pasting system |
| 41 | PP | 1986-62853 | Method of hardness inspection during thermosetting resin curing process |
| 42 | PP | 1986-69826 | Polyglycidyl ether production method, and resins producible from polyglycidyl ether |
| 43 | PP | 1986-103960 | PMR-type polyimide resin varnish |
| 44 | PP | 1986-114848 | Metal group composite production method |
| 45 | PP | 1986-130439 | Composite wire production method |
| 46 | PP | 1986-138622 | Fiber reinforced composites and hardened moldings produced from them |
| 47 | PP | 1986-139762 | Device for detecting electrical properties of resins |
| 48 | PP | 1986-141724 | Composition of polyglycidyl ether |
| 49 | PP | 1986-179220 | Method of producing epoxy resin containing imide resin |
| 50 | PP | 1986-179233 | Polyimide based prepreg |
| 51 | PP | 1986-186375 | New polyepoxy compound |

[continued]

[Continuation of Table 1]

| | | | |
|----|----|-------------|---|
| 52 | PP | 1986-199933 | Method and system for continuously fabricating carbon fiber reinforced plastic pipes |
| 53 | PP | 1986-205114 | Composite material molding method |
| 54 | PP | 1986-218623 | Epoxy resin composition and hardener |
| 55 | PP | 1986-223021 | Prepreg production method |
| 56 | PP | 1986-223022 | Composition of curing resin |
| 57 | PP | 1986-225164 | Aromatic polyamine containing imide group, and production method |
| 58 | PP | 1986-232999 | Composite environment testing system |
| 59 | PP | 1986-235373 | Continuous lamination system |
| 60 | PP | 1986-233000 | Testpiece setting device for composite environment testing system |
| 61 | PP | 1986-235374 | Winding device |
| 62 | PP | 1986-276823 | New thermosetting end-capping agent |
| 63 | PP | 1986-277681 | Addition-curing quinoxaline resin oligomer, and fiber-reinforced composite preform produced from it |
| 64 | PP | 1986-290038 | Automatic method and device for FRP tape pasting |
| 65 | PP | 1987-53324 | Prepreg production method |
| 66 | PP | 1987-54720 | Polyepoxy compound production method |
| 67 | PP | 1987-68605 | Composite material production method |
| 68 | PP | 1987-103109 | Metallic mold for synthetic resin molding |
| 69 | PP | 1987-105608 | Metallic mold for synthetic resin molding |
| 70 | PP | 1987-119027 | Continuous molding method for reinforced plastic pipe production |
| 71 | PP | 1987-132637 | Method and system for fabricating fiber reinforced plastic cylinders by drawing |
| 72 | PP | 1987-134223 | Liquid resin sealing mechanism |

[continued]

[Continuation of Table 1]

| | | | |
|--|----|-------------|--|
| 73 | PP | 1987-134224 | Thermosetting resin injection system |
| 74 | PP | 1987-139837 | Metal matrix composite production method |
| 75 | PP | 1987-144927 | Automatic method and device for FRP tape pasting |
| 76 | PP | 1987-170403 | Mold for hot isostatic molding |
| 77 | PP | 1987-184809 | Injection head for resin injection |
| 78 | PP | 1987-187019 | Method of fabricating fiber reinforced plastic cylinders by drawing |
| 79 | PP | 1987-192656 | Acoustic emission signal discriminating device |
| 80 | PP | 1987-222846 | Long-fiber/metal composite production method |
| 81 | PP | 1987-244621 | Method and system for continuously fabricating carbon fiber reinforced plastic pipes |
| 28 patents pending, in addition to the above | | | |
| 1 | UT | 1984-144460 | DC electric resistance measuring apparatus for thermosetting resin based composites |
| 2 | PP | 1985-119055 | Automatic FRP tape cutting device |
| 3 | PP | 1986-175420 | Construction of metal mold for resin molding |

Table 2. Examples of Computer Programs Developed in Joint R&D Project

1. Strength, rigidity, and flutter optimization program (revised version)
"COSMOS59-SAP"
2. Frequency optimization program "COSMOS59-FREQUENCY"
3. Buckling optimization program "OPTBUCKL"
4. Strain-rate dependent type structure equation program for FRM
"CE-COMPOSITE"
5. Strain-rate dependent type structure equation program for laminar FRM
"CONFL"
6. Automatic detection and analysis program for curing reaction signals
(revised version)
7. Basic program for automatically discriminating molding crack signals
"DATAIN.BAS," "AEANLY.BAS"

(4) Significance of R&D on Metal-Matrix Composite Materials

In this country, R&D on metal-matrix composite-materials, other than those for cemented carbide tools which have a long history, referred to as MMC or FRM, started in the first half of the 1970's with the aim of developing materials for use mainly in the fields of nuclear power development and audio equipment. After the first oil embargo by Arab nations, research work to develop composite materials which can reduce the weights of automotive engines was actively promoted. Subsequently, a patent application boom occurred and it peaked around 1983. Through these developments, the research and development of metal-matrix composite materials in Japan has come to gain worldwide attention.

However, as far as R&D in lightweight, structural metal-matrix composite materials is concerned, Japan has been lagging behind other advanced countries partly because the domestic market for such materials has been slow to develop. In the present research program, R&D efforts will be centered on metal-matrix composite materials reinforced with long fibers, particularly, fine ceramic fibers produced by baking polymer synthetic fibers, so that the applications of fine ceramic fiber techniques, at which this country is strong, will be promoted and also so that metal-matrix composite materials suitable for use as lightweight structural materials will be made available.

20109/9365

High Performance FRM Wire Preforms Developed

43063802j Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 66-68

[Article by Akira Koyama, Department of Materials Science, Tokyo University: "R&D of High Performance Wire Preforms for C/Al and SiC(Nicalon)/Al FRMs"]

[Text] **Abstract:** In the past several years the Japanese community of composite materials research has expended extensive effort developing industrial bases to produce composite materials for future industries. This paper provides recent results and status of the high performance wire preforms for carbon fiber (Torayca T300, M40) or silicon carbide fiber (Nicalon) reinforced aluminum matrix composite materials. This is a brief review of the work performed as part of the national project under management of the Research and Development Institute of Metals and Composites for Future Industries.

Microstructural evolutions and mechanical property changes during fabrication process of FRMs and in service degradations including nuclear reactor environments are discussed.

1. Introduction

The national project being administered by the Research and Development Institute of Metals and Composites for Future Industries features a program for developing high-performance composite materials (FRM [fiber-reinforced materials]). In the program, research work for developing techniques for producing the wire preforms, which are extremely useful, for aluminum matrix composite materials reinforced with carbon fibers or silicon carbide fibers has been promoted. For this research program, high-elasticity, high-strength carbon fiber ("Torayca" produced by Toray Industries), and PCS silicon carbide fiber ("Nicalon" produced by Nippon Carbon) have been adopted as the reinforcement fibers and integrated research on techniques for producing high-flexibility, high-performance wire preforms has been conducted. The target values of wire preform properties set for this research program have already been achieved by the techniques so far developed. In this paper, the present state of the research work being made on the production of carbon fiber preforms (Toray Industries is in

charge) and silicon carbide preforms (Nippon Carbon is in charge) by the continuous infiltration method will be reported and the joint research work being made for fiber improvement (undertaken by the Government Industrial Research Institute, Osaka), and material interface quality improvement (undertaken by the Department of Materials Science of the University of Tokyo) will be described

2. Carbon-Fiber Wire Preforms

In the research work for the production of carbon fiber wire preforms, a process comprising two continuous steps, one for coating high-strength, high-elasticity PAN-based carbon fiber by the CVD method and the other for producing wire preforms by the infiltration method, has been studied. As a result, a technique which enables about 300 m of wire preform with a fiber volume fraction of about 50 percent to be continuously produced has been established. High-strength preforms whose tensile strength exceeds 1.6 GPa at room temperature or 1.4 GPa at 450°C have been produced using the technique (Table 1, Figure 1). As the wire-preform production process has been improved the production speed and the product property stability have also been drastically enhanced.^{1,2} In addition, a new coating method in which carbon coating is made by means of pyrolysis using propane is presently under study. Through the study, improvement is being made regarding the inhibition of interface reactions and the wettability of C/Al.³ Progress is also being made in improving the properties of wire preforms which are dependent on the interface structure and various strength properties.⁴

Table 1. Tensile Strength of C/Al and SiC (pcs)/Al Preform Wires Fabricated by Liquid Metal Infiltration Method

| Reinforcing fiber/matrix | | V _f (%) | Specific gravity | Tensile strength (MPa) | | |
|--------------------------|------------------------|--------------------|------------------|------------------------|-------|-------|
| | | | | R.T. | 573 K | 723 K |
| C/Al | T300 (C coated)/A6061 | 45 | 2.18 | 1,580 | 1,530 | 1,310 |
| | T300(SiC coated)/A6061 | 32 | 2.38 | 710 | 750 | 670 |
| | M40-S /A5056H | 51 | 2.22 | 1,520 | 1,500 | 1,460 |
| | M40-U /A6061 | 50 | 2.26 | 1,490 | | 1,440 |
| | M40-S /A1080 | 45 | 2.30 | 1,170 | 1,110 | 1,110 |
| | M40J-S/A1080 | 45 | 2.28 | 1,330 | 1,340 | 1,470 |
| SiC | | | | | | |
| (pcs) | NLM-200/Al-5.7%Ni | 50 | 2.60 | 1,690 | | 1,690 |
| /Al | NLM-200/Al-0.2%Ti | 50 | 2.60 | 1,580 | | 1,380 |

3. Silicon Carbide Fiber Wire Preforms

Various techniques for producing, by the continuous infiltration method, wire preforms containing Nicalon fibers, which are SiC fibers obtained by baking polycarbosilane, have been studied. The prime feature of the preform production process developed is that it eliminates the need for fiber surface treatment--a process which used to be regarded as essential

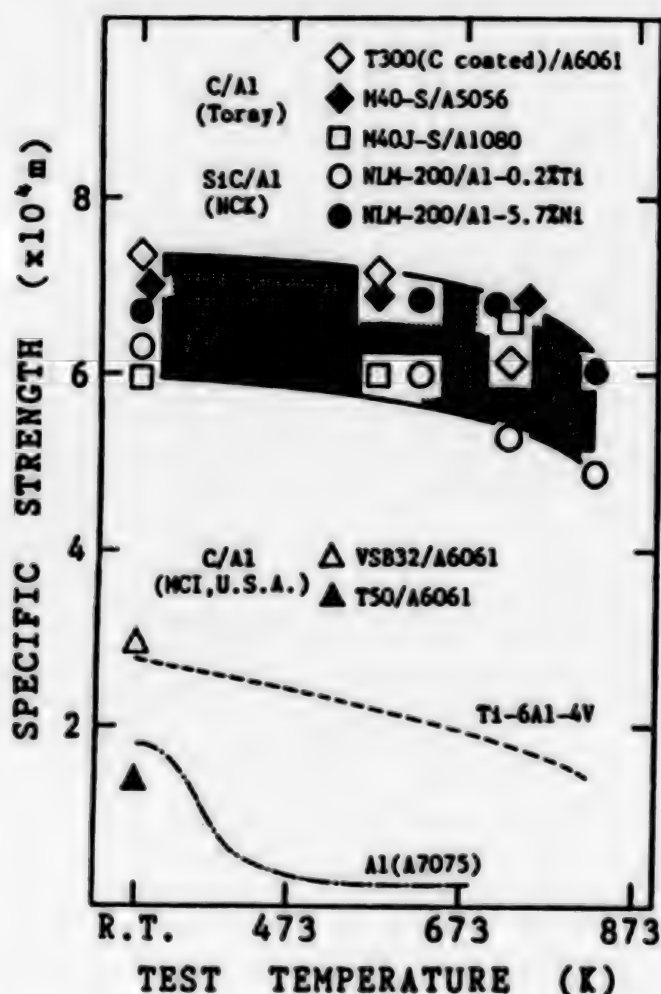


Figure 1. Dependence of Specific Strength of C/Al and SiC(pcs)/Al Preform Wires on Test Temperature

for the production of SiC/Al preforms--by making the most of the features of the Nicalon fiber. This process in which the conditions for preform production are optimized enables the production of stable-quality, high-strength wire preforms. In fact, the process makes it possible to produce Al050-matrix preforms having a room-temperature strength of 1.5 GPa or more, as shown in Table 1 and Figure 1. The Weibull coefficient measured 27 on samples produced by this process. Thus, it has been shown that the materials produced using the process offer high reliability. Furthermore, adding 5.7 percent of nickel to the material causes the matrix to be converted into an eutectic composite material. The composite materials produced in that way recorded high strength values, close to 1.7 GPa both at room temperature and at 450°C.^{5,6} The wire preforms produced using these techniques show exceptionally high and stable resistance against heat and irradiation. It has been shown that potentially they can be used as nuclear reactor materials. To study their properties, their microstructures have been analyzed using electron microscopes or field ion microscopes, or by conducting simulated electron and ion irradiation tests. As a result, it has been shown that they have possibilities of being further enhanced in terms of elasticity and strength.^{4,7-9}

4. Conclusion

The target property values set for the development of high-performance preforms in the next-generation, composite material development project are very high. With the aim of achieving the targets, research work on an advanced continuous process for producing high-performance preforms containing reinforcement fibers developed in Japan began and, eventually, an advanced process, to which there is no parallel in the world, for wire preform production has successfully been developed, as a fruit of cooperative research efforts by private enterprises, national laboratories, and universities under the leadership of the Research and Development Institute of Metals and Composites for Future Industries. Besides the development of the process, the research program has borne many other fruits. Thus, the outcome of the research program can be said to have great significance from the viewpoint of establishing metal-matrix composite materials as practical materials. It is hoped that another national project effective in facilitating the further progress of research and development in this area will be introduced.

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Latest Fabrication Process for Metal-Matrix Composites

43063802k Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-23 Mar 88 pp 69-73

[Article by Akira Sakamoto, Nagoya Aircraft Works of Mitsubishi Heavy Industries, Ltd.: "Development of Fabrication Process for Metal-Matrix Composite Materials"]

[Text] **Abstract:** Research and development work of metal-matrix composites has been performed since 1981, being sponsored by Agency of Industrial Science and Technology, MITI. This paper presents a review of the latest status of development of fabrication process and technology for MMC, covering the following items:

- Fabrication of C(M40)Al and SiC (Nicalon)/Al using wire-preform developed in this program.
- Development of high temperature Al alloy matrix composites fabrication of MMC by hot isostatic pressing [HIP] using powder metal preform.
- Process development of fabrication for MMC with laser beam

1. Introduction

The MMC [metal-matrix composite] materials and MMC forming processes being studied for the next-generation material development project and the organizations undertaking the research are listed in Table 1. The research work for the development of wire preform forming processes ^{1,2} is aimed at establishing forming processes suitable for the two types of wire preforms^{3,4} under development by the material development group working for the same project. In this work for a forming process for materials containing CVD-processed fiber, attention is paid to the relationship between the mechanical characteristics, particularly, the high-temperature characteristics of the materials and their matrix-alloy composition.^{5,6} As for the process for MMC forming by HIP [hot isostatic pressing], a method in which matrix-metal powders are used has been adopted so as to facilitate near-net-shape forming and raise the degree of freedom in matrix-composition control.^{6,7}

Table 1. Typical MMC Material Systems and Fabrication Process Under Research

| Material system | Fabrication process | | Research organization |
|----------------------|--|-----------------------------------|--|
| | Preform | Consolidation method | |
| M40/5056 | wire | hot pressing | Mitsubishi Heavy Industries, Ltd. |
| M40/5056 | wire | hot rolling | Fuji Heavy Industries, Ltd. |
| C/Al M40/5056 | wire | laser heating and rolling | Mitsubishi Electric Corp. |
| M40/6061 | green sheet | liquid phase pressing | Mitsubishi Heavy Industries, Ltd. |
| HM40/4032 | powder slurry | HIP | Kawasaki Heavy Industries, Ltd. |
| Nicalon/1050 | wire | hot pressing | Fuji Heavy Industries, Ltd. |
| Nicalon/1050 | wire | hot pressing | Mitsubishi Heavy Industries, Ltd. |
| SiC/ Nicalon/1050 Al | wire | laser heating and rolling | Mitsubishi Electric Corp. |
| SCS-2/6061 | green sheet | hot pressing | Ishikawajima-Harima Heavy Industries Co., Ltd. |
| SCS-2/Al-4Ti | LPP spray sheet | hot pressing | |
| SCS-6/Ti6Al4V | green sheet | hot pressing | Ishikawajima-Harima Heavy Industries Co., Ltd. |
| SiC/ Ti | SCS-6/Ti6Al4V powder sheet Ti6Al2Sn4Zr6Mo | HIP | Kobe Steel, Ltd. |
| SiC whisker/Al | green | squeeze casting and hot extrusion | Mitsubishi Heavy Industries, Ltd. |

The development of a laser beam forming process is being advanced with the aim of making it possible to turn MMC wire preforms into thin sheets for use in space structures.⁸

For the forming of SiC whisker/Al materials, the squeeze casting-extrusion method has been selected as the research target. As a result of reducing source-material defects and improving matrix-alloy composition, MMC materials having a strength on the order of 1,000 MPa have already been successfully formed by the method. All the forming processes mentioned above make either heating or pressing. The processes are carried out at high temperatures. Therefore, in order to carry them out successfully, it is important to optimize the process parameters from the viewpoint of inhibiting the reactions at fiber/matrix interfaces and achieving dense

material composition. Some of the results of the MMC forming process development work will be introduced in the following.

2. Wire Preform Forming

To form wire preforms of C/Al (M40/5056) or SiC/Al (Nicalon/1050) into a good composite, it is necessary to carry out the forming process at a temperature coming right on the solidus of the matrix metal. If they are formed at a temperature exceeding 823 K, Al_4C_3 is generated at the fiber-matrix interfaces to cause their formed-state strength to be reduced. To solve this problem, it is necessary to form them by applying higher pressure at a lower temperature.

In roll forming, the plastic flow of the matrix metal caused by a high stress that is generated when the material is pressed by the rolls is utilized. Therefore, roll forming is suitable for high-pressure, low-temperature forming. Nicalon/1050 samples formed at 773°C recorded strength in the 0° direction equal to or exceeding 95 percent that of the preforms. Their strength in the 90° direction reached 97 MPa. These values are of a high level for material of this type.

For press forming, a new process has been developed. In the new process, alloy foil whose solidus is lower than that of the preform matrix is pressed together with the preform. The alloy foil causes partial and temporary liquid-phase formation in the preform even at a low temperature. Therefore, it results in improved formability without requiring the forming pressure to be raised. High-performance samples have been formed from wire preforms of the two types of materials through a forming process made at 803 K and using the foil of 2017 (with a solidus of 785 K and a liquidus of 842 K).

3. Development of Heat Resistant Al-Matrix Composite Material

In connection with the SiC fiber having a CVD-processed carbon fiber core, a forming process for aluminum- and titanium-matrix composite materials is now being developed. In this section, the composites of SiC fibers and heat resistant aluminum alloys will be discussed.

Two types of composites have been developed: one type consisting of a heat resistant aluminum alloy, Al-8Fe-4Ce, as the matrix and the SiC fiber (SCS2), which is used to produce aluminum-matrix composite materials, and the other type consisting of another heat resistant aluminum alloy, Al-4Ti, as the matrix and the SiC fiber. These composites are produced using a multilayer preform production technique in which LPPS (low-pressure plasma spraying) is made. In the new process, heat resistant aluminum alloy powder is sprayed over a backing foil by the LPPS method, then fiber is wrapped around the backing foil, and LPPS is made again. This process is repeated to produce a multilayer preform. Composite samples with a Vf value of 48 percent have been formed by stacking preforms produce in the above way and hot-pressing them at 873 K and 33 MPa so as to remove the defects generated by thermal spraying and make diffusion-joining.

Samples of Al-4Ti-matrix composite materials formed using the above-described procedures showed high strength at elevated temperatures. Their strength in the 0° direction does not decline at 573 K. Even at 723 K, they retain 95 percent of their strength at ordinary temperature. In specific strength, they exceed SCS6/Ti-6Al-4V which is a Ti-matrix composite material.

4. MMC Forming by Powder HIP Method

For the forming of C/Al composite materials, a HIP process in which powdery slurry preforms are pressed has been developed. Compacts whose strength at ordinary temperature exceeds 1,000 MPa were produced from HM40/4032 by the HIP process. Cylindrical sales have been produced from the compacts. It has been confirmed that the HIP method is effective also for molding wire preforms into cylinders.

For the forming of SiC(CVD)/Ti composite materials, a HIP process in which laminates of matrix-metal powder sheets and fiber mats (made of fiber arrays fixed with resin) are pressed, has been developed. Fairly good compacts of SCS6/Ti-6Al-2Sn-4Zr-6Mo and SCS6/Ti-6Al-4V have been produced using the HIP process. This process can be used to mold alloys which are not available in foil form. Therefore, this process allows a greater freedom in matrix selection for MMC materials and is usable in molding high-strength alloys or intermetallic compound-matrix composite materials.

5. Development of laser Process for Thin-Plate Forming

Through the observation of wire preforms being irradiated with a laser beam whose energy density is relatively low, it has been found that, when a metal-matrix composite material is irradiated with a laser beam, there can occur a condition in which only the matrix metal is fused while the reaction between the laser beam and the fiber is held to a minimum. It has been confirmed that a thin MMC plate can be obtained by irradiating a number of wire preforms with a laser beam in the above-described condition and then rolling them immediately.

6. Conclusion

The relationships between the specific strength and specific modulus of the MMCs formed using the foregoing techniques are shown in Figure 1. The temperature dependence of their specific strength is shown in Figure 2. What are dealt with in these figures are the characteristics in the 0° direction of the unidirectionally reinforced MMCs, so that the MMCs cannot directly be compared with the conventional structural metals based only on these figures. Moreover, there are many problems with the MMCs yet to be solved, for example, variations in their characteristics and problems concerning their anisotropy. Still, it can be said that the MMCs have characteristics far superior to those of the conventional structural metals.

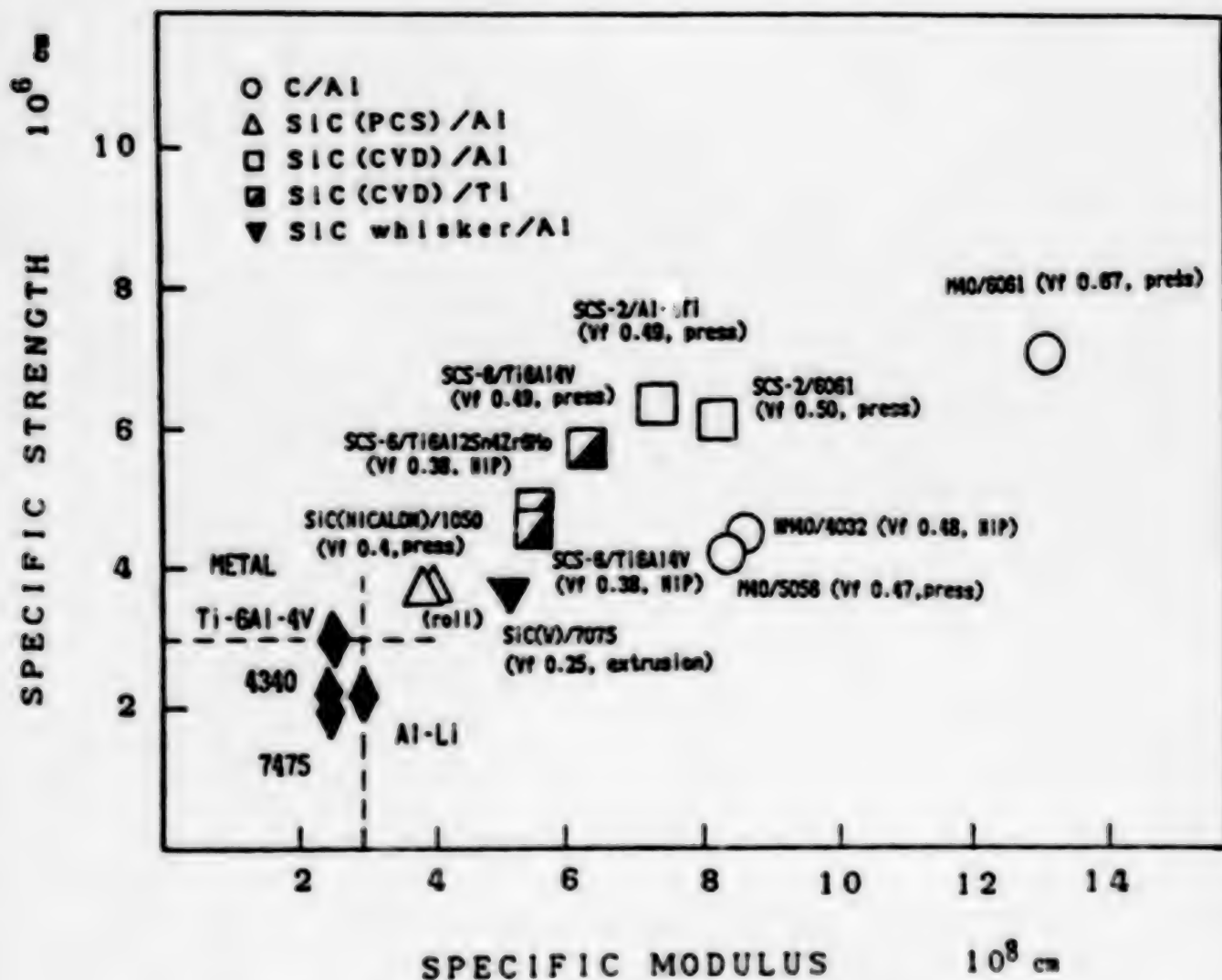


Figure 1. Specific Strength Versus Specific Modulus

The aluminum-matrix composite materials show little reduction in their strength at temperatures up to 723 K. Some of them exceed the titanium-matrix materials in specific strength. Along with the titanium-matrix composite materials they will also prove useful as light, heat resistant materials usable not only in aircraft engines but in such next-generation aircraft as SSTs, HSTs, and space planes which are required to withstand aerodynamic heating.

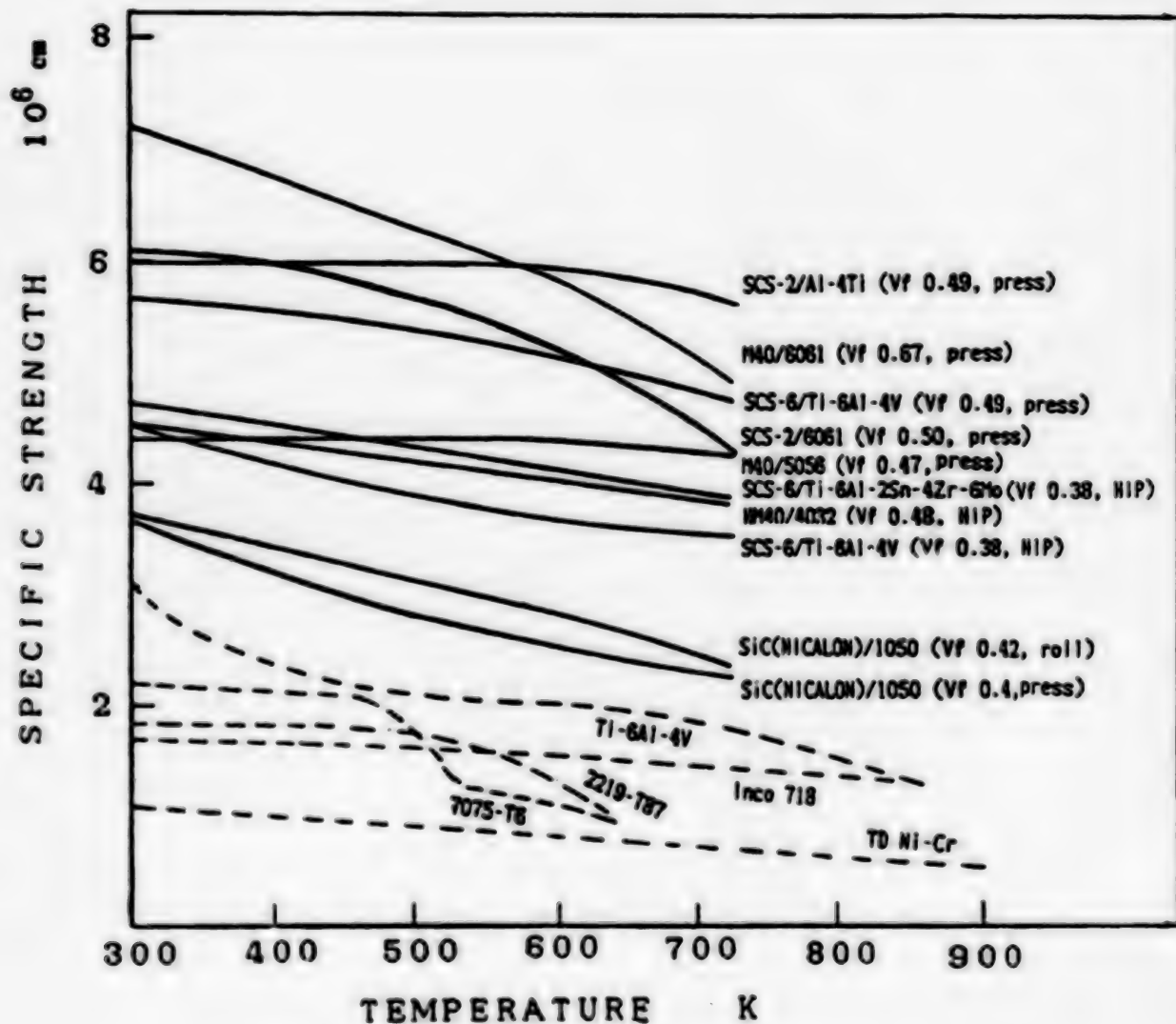


Figure 2. Specific Strength Versus Temperature

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Continuous Preform Wire Production, CVD Process

430638021 Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 74-76

[Article by Takakazu Suzuki, Industrial Products Research Institute, Agency of Industrial Science and Technology, MITI: "Production of Preform Wire for C Fiber/Al Composite Material by LPMOCVD"]

[Excerpt] **Abstract:** The present research work is aimed at making it possible to uniformly and tightly coat pitch-based carbon fiber yarns with aluminum by the reduced-pressure CVD [chemical vapor deposition] method using an organic aluminum compound as a source material without causing fiber degradation and to continuously produce a preform for a carbon fiber-reinforced aluminum composite material with a high fiber-content ratio (Vf). The CVD process in which an organic aluminum compound is used as a source material enables carbon fiber to be coated with aluminum at a temperature for below the melting point of aluminum. In addition, the throwing power obtained in the process is much greater than that obtained in the PVD method. In fact, with the CVD process, it is possible to deposit aluminum even inside the fiber yarns. The oriented crystal structure on the surface of pitch-based fiber makes the fiber reluctant to react with aluminum. As compared with the atmospheric-pressure CVD method, the reduced-pressure CVD method enables highly uniform thin film to be formed, the film thickness to be easily controlled, and thin-film properties (e.g., density) to be improved. Having these features, the reduced-pressure CVD method is thought to enable the production of high-performance fiber-reinforced metals (FRMs).

At the present symposium, the continuous vaporize-deposit wire production method will be outlined and problems with the method will be discussed.

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Problems, Potential of MMCs Outlined

43063802m Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 77-79

[Article by Sokichi Umekawa, Science University of Tokyo: "Problems and Potential of MMCs"]

[Text] **Abstract:** Because of the various excellent characteristics of metallic materials, the MMC have been expected for wide applications in engineering. Among the MMCs, the dispersion strengthened metals like SAP and other ODS materials and the particle reinforced composites such as refractory hard metal or cermet, have been developed for a long time and currently in an overmaturity state. The FRM, on the other hand, is much younger than those two types of MMC and still developing for the advanced applications. Nevertheless, a high potential and attractive features are expected, current status of the FRM is not always satisfied. Following an overview of those topics, the intrinsic problems of the FRM, the interfacial phenomena which are accompanied by a large scatter of the strength data, for example, are discussed. Finally, a possible solution for the problem and prospects for utilizing the high potentials of FRM for the nonstructural and structural applications are proposed.

The development of FRP's [fiber-reinforced plastic] and FRP-based composite materials has been continuing since the 1940's. Today, they, as industrial materials, hold decisively predominant positions in many fields. As for the FRMs [fiber-reinforced metals], on the other hand, the results of research work started being reported in the first half of the 1960's. Some of the MMCs have an even longer history than that of the FRPs. Nevertheless, the number of practical applications of MMCs is still small. This paper will give an overview of problems with and the potential of the MMCs.

1. Expectation Put on MMCs

A feature of the MMCs is that they have metallic properties. First, it is well known that metals, while having high elastic moduli, also have considerable strength. As compared with other materials, metals have a notable feature that the differences in properties among the same type of metals are small. This feature enhances the reliability of metals as industrial materials. Metals, which may be alloys, produced with a certain

composition and under designated process conditions show nearly identical modulus and strength values, regardless of where or by whom they are produced. The values of their properties can be treated as material constants. Second, metals generally have high ductility and fracture toughness. Their high ductility is a major factor in their high reliability and constitutes a great advantage as compared with other materials whose strength is, in many cases, evaluated only in terms of single categories of strength such as bending strength and compressive strength. Their high fracture toughness is, needless to say, a factor in their behavior against racking. Their nonstructural factors such as the effects of alloying or heat treatment, their characteristics at high temperatures, and their electric, magnetic, thermal, and chemical properties also make up many of their features that have contributed toward keeping them, including alloys, in use as the primary industrial materials for both structural and nonstructural applications. The structural MMCs include ODS materials such as SAP and TD Ni-Cr, which are dispersion-strengthened materials, and particle-reinforced composites such as WC, TiC, and TaC, which are among the cemented carbides or cermets formed using metallic binders. These composite materials have a long history and they have been used in many fields. Therefore, they cannot necessarily be regarded as the principal targets of current R&D work. Rather, it is the FRMs and associated composite materials that are likely to draw the most attention as the MMCs to be used from now on.

The FRMs are expected to offer merits attributable to the features, particularly the ductility and high-temperature characteristics, of their matrix metals. It is also encouraging with regard to the prospects for FRMs that various fibers ranging from whisker to CVD-processed fibers have a great potential as reinforcements for many materials including graphite, SiC, Al_2O_3 , and B. As for the UDS-based materials, there are various reasons why we do not have great expectations for them. However, the techniques for controlling their matrix-phase texture will be useful as fundamental techniques for material property improvement.

2. Strength and Its Variation

Variations in the strength of FRMs constitute one of the weak points. Many of the fibers making up the reinforcement phases in FRMs are inorganic and brittle. Such fibers incorporate many more variation factors than do metals. Their strength is largely affected not only by their constituent elements but also by their microscopic or macroscopic structures--for example, the ratio between the amounts of crystalline substances and the sizes and distributions of the respective substances--the sizes and distribution of defects, and many others. The "characterization" criteria set for evaluating their characteristics are not sufficiently effective; such criteria are seldom used for metals. When an external force is applied to an FRM, large portions of the force are borne by the fibers contained in the FRM. Therefore, variations in strength between the fibers directly affect the strength of the FRM. Among different fibers, the whisker is particularly difficult to control in producing FRMs. When the whisker fibers are used as a reinforcement, the orientation and dispersion in the FRM must be properly controlled. Moreover, their texture, crystal

orientation and structure, microstructure--particularly surface microstructure--and dimensions are also factors causing variations in their strength.

Furthermore, various factors involved in the fabrication of FRMs constitute decisive factors in causing variations in their strength. Particularly, the interfaces between fibers contained in an FRM and its matrix phases are greatly affected by the fabrication method and conditions. These are the reasons why a factor such as the Weibull coefficient that can almost be ignored in evaluating metals is included in the important factors on which FRMs are evaluated. To cope with the problem of FRM strength variations it is hoped that a practical and effective method of inspecting their strength will be developed. For FRMs, sample inspection is not reliable enough. It is desirable that they undergo nondestructive inspection on an overall quantity basis. Therefore, establishing a method to evaluate the exterior and interior, microscopic and macroscopic texture and structure of FRMs is an extremely important industrial task to be tackled.

3. Interface Problems

The interface problems with the FRMs include mainly those associated either with the bonding between fibers and matrix phases or with the physical or chemical reactions between them. The two types of problems are closely interrelated. Solving the interface problems may be said to be the key to development of FRMs. The interfaces between fibers and matrix phases formed in FRMs are of a totally different nature from those formed in FRPs. In an extreme case, it may even be said that the plastics constituting matrix phases in FRPs are akin to adhesives, while, in FRMs, the metals constituting the matrix phases serve as the brazer for binding inorganic substances. Bonding is a simple mechanical process. Bonding strength is generally considered to be directly dependent on the so-called wetting properties of the materials involved or the angle at which the liquid phases contact the solid phases, setting aside the so-called anchoring effect or the clamping effect caused by the thermal residual stress. Bonding in an FRM is, in reality, much more complicated. The factors by which it is greatly affected include the magnitudes of reactions between the solid and liquid phases, the shapes and dimensions of solid-phase fibers, their curvatures, the physical or chemical conditions of their surfaces, and the temperature, pressure, and vibration to which the FRM is subjected. At any rate, for FRMs, bonding is a necessary condition to be met to make effective use of the strength of fibers. The reactions that occur between the solid and liquid phases mostly comprise diffusion or chemical reactions. Such reactions erode fiber surfaces to cause them to deteriorate and interface layers to be formed between fibers and matrix phases. Generally, interface layers are brittle and tend to permit stress concentration, so that they are very likely to make themselves the nuclei of destruction. The reactions, on the other hand, intensify the bonding strength between the fibers and matrix phases. It is said that, where the foregoing phenomena occur in an FRM, there is an optimum interface-layer thickness at which the FRM thickness is maximized. However, with many other factors which affect the FRM strength, such an optimum thickness, have not been defined. The reactions, as well as bonding, between solid

and liquid phases are complicated phenomena which occur not only in the fabrication process but also while the fabricated composite materials are in use. Therefore, it is extremely important to properly control the reactions. At present, appropriately treating fibers, in particular coating them, is thought to be an effective way of controlling the reactions. Among the same type of FRMs, the rate of increase in the thickness of interface reaction layers under a certain condition is estimated to be nearly constant. Therefore, it can be said that, where fibers have larger diameters in an FRM, the effect on the FRM of the reaction layers, particularly the property degrading effect, is smaller. The merit of thick fibers such as those processed by CVD cannot be ignored. The critical lengths of fibers in FRMs range from 10^1 to 10^2 at ordinary temperature unless the FRMs are placed under extremely adverse conditions. The relatively small critical fiber lengths are thought to be attributable, even if the bonding strength between fibers and matrix phases is not adequate, to the matrix phases being caused to clamp fibers as the temperature lowers.

4. Potential of MCCs

The problems involved in the practical use of FRMs have been briefly discussed. This may be said to fall within the realm of common knowledge today. However, when one is put in a position to actually handle metals or inorganic fibers, he will, in many cases, find himself bogged down in meaningless information without being able to locate any literature which may be regarded as a "superior data" or any systematic data like that obtained by making proper computerized simulations. With regard to the interface problems, there is a large gap between the extent to which theoretical studies have been made and the availability of the corresponding data obtained by carrying out experiments. For example, high-strength materials which have not even undergone adequate fatigue tests or materials which have been developed for use at high temperature but on which almost no creep data is available will still have to go a long way before they can be practical structural materials. "Superior data" on FRMs, if made available, can show the potential of FRMs and may be useful in considering special applications for which the material cost does not matter much. From the viewpoint of industrial applications of FRMs, however, reducing property variations should be the present prime target. As far as the fiber strength is concerned, mass production is a solution. In fact, glass fibers no longer pose property-variation problems. In the same regard, carbon fibers have also been improved considerably. Setting aside the cost problem, which is a great obstacle to the development of FRMs as practical materials, will it be possible to solve the interface problems with the FRMs in a similar way? The prospects are very bright for nonstructural FRMs as opposed to structural FRMs. This is because the factors in nonstructural FRMs are thought to be relatively insensitive to the internal structures of the FRMs. Great hope can be placed on such FRMs that have superior electric, magnetic, thermal or chemical properties, or other properties having nothing to do with large deformation or destruction, or combinations of such properties.

Present State of Advanced Plastic Composite Materials

43063802n Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 81-84

[Article by Hiroshi Maki, Takusvoku University: "Status of Advanced Plastic Composite Materials in Japan"]

[Excerpts] **Abstract:** The "Composite Materials," theme in the R&D Project of Basic Technology for Future Industries sponsored by the Agency of Industrial Science and Technology, MITI, shall be finished in March 1989. This theme has already brought about many excellent results up to now. In the last few years, many Japanese companies have been researching and developing advanced reinforcements, e.g., pitch CF. They have been scrutinizing the business plan of such reinforcements. At present they are forced to make a grave decision whether they should industrialize them or not. Their worries are marketing research, demand and supply balance, and so on. After a brief presentation on progress of the CFRP and the advanced FRP, the present status and the problems awaiting solution are given.

In 1981, the Ministry of International Trade and Industry inaugurated the Next-Generation Industrial Basic Technology Research and Development System. Coordinated fundamental research on advanced composite materials was begun as one of the 12 research programs set under the system. The research targets covered by the composite material research program include FRPs, FRMs, quality evaluation techniques, and design techniques. The results of research on quality evaluation techniques, design techniques, and FRMs were reported in the morning session. The present report is going to be followed by a report on the results of FRP research.

Government Industrial Research Institute, Kyushu, developed pitch-based CF by the premesoprase method in 1981. Stimulated by the introduction of the aforementioned mesoprase method and the premesoprase method, many enterprises in different industries such as the chemical industry, iron and steel industry, and oil refinery industry started positive research for the development of pitch-based CF which can be commercialized. Such enterprises are said to total about 30. Of these, Kajima Sekiyu commercialized pitch-based HPCF in 1985 and Mitsubishi Chemical Industries followed in 1987.

The Agency of Natural Resources and Energy set up a committee, made up of about 10 oil refining companies, in the oil industry activation center [sekiyu sangyo kasseika senta] in 1986, and, through cooperation from various industries, started research for the development of pitch-based CF applications, particularly, in automobiles and buildings.

2. Present State of Advanced Plastic Composite Materials

Among different types of advanced composite materials, the CFRP containing PAN-based HPCF is most used. The consumption of CF in Japan alone is estimated to have totaled about 700 tons in 1987. The domestic demand for CF is broken down into: about 67 percent for use in space and aeronautical equipment, about 80 percent for use in sporting goods or amusement equipment, and about 14 percent for use in other products. This breakdown largely differs from that in the United States or Europe. In spite of the great efforts being made by the enterprises concerned, research work for the development of CF applications in the fields of automobiles and buildings has made little progress, being confronted by an extreme difficulty. The toughest problem is the high cost of CF. At present, the disclosed production capacity of the CF producers totals 3,350 tons of PAN-based CF and 1,012 tons of pitch-based CF (including 900 tons of GP-grade CF). It is expected that, from now on the production of pitch-based CF will increase faster than that of PAN-based CF. At present, a great worry to the industry of advanced fiber-reinforced materials is the unbalanced supply-demand condition. In other words, the industry is under the pressing need to develop more applications for fiber-reinforced materials.

Under such circumstances, the walls made of CFRC that were used in the intelligent building (named Ark Hills Building) constructed by Kajima Corp. at Roppongi, Tokyo, in 1986 and the FRP developed by Shimizu Construction Co. as a material to replace iron reinforcing rods used in civil engineering and construction works gained great attention.

Engineering plastics used mainly in the field of injection molding were developed at almost the same time in Japan, the United States, and Europe. According to a survey made by MITI, the supply of engineering plastics in Japan (including those supplied through imports or for export) totaled 251,000 tons in 1978 and 445,000 tons in 1983. That is, the supply increased as much as about 1.8 times in the 5-year period. However, for the supply to reach that level, it took as long as about 20 years after the introduction of engineering plastics in the market. Of the total amount of engineering plastics in 1978, 21 percent or more were supplied in the form of composite materials. The ratio was about 38 percent for 1983; that is, about 167,000 tons of engineering plastics were supplied as composite materials in 1983. Of the composite materials supplied in 1983, as much as 72,000 tons were comprised of FRTPs and hybrid FRTPs. This amount accounts for about 16 percent of the total amount of engineering plastics supplied in the year. It is estimated that CFRTPs accounted for most of the FRTPs supplied that year. Recently, the supply of FRTPs is estimated to be about 150,000 tons of CFRTPs and about 600 tons of CFRTPs. The CFRTP market is still small, but it is expected to grow in the future.

As for long-fiber FRTPs, the development of the technique for processing unidirectional CF/PEEK [polyetheretherketone] has been among the research targets set for the next-generation industrial basic technology research and development project. High hopes are placed on the CF/PEEK, but there are many relevant technical problems yet to be solved.

The consumption in Japan of Aramid fiber is estimated at about 200,000 tons a year (world consumption totals 14,000 tons). Of the total domestic consumption, 70 percent is thought to be used for FRRs. Kuraray Co. appears to be considering the commercialization of Vectoran (liquid-crystal aromatic polyester fiber).

3. Problems With Advanced Plastic Composite Materials Awaiting Solution

These days, technology progresses very rapidly, resulting in enhanced product performance and functions. This is not limited only to the fields of most advanced technologies. In close association with such a trend, the expectations placed on advanced materials have been growing larger and they have been required to meet increasingly extensive requirements. In such a situation, advanced FRPs are among the advanced plastic composite materials which are regarded as having very bright prospects. Even though great expectation is placed on the advanced FRPs, that expectation, for the most part, is not yet concrete. The latent demand is not based on concrete ideas, either. There is some real demand, but it is still small as discussed in the foregoing.

To enable a new material to be established as an industrial material, it is essential that the market be established along with the production technique.

Under the Next-Generation Industrial Basic Technology Research and Development System, many elementary techniques for the production of advanced composite materials have been developed. However, when the future market for advanced composite materials is considered, it is noted that there are still many technical problems to be solved. Particularly, the composite material fabrication processes assume great importance. When the history of the development of engineering plastics is considered, it is important to enhance the reliability of fabrication techniques and significantly shorten the molding cycle. It is further necessary that the development of technologies be promoted mainly by private enterprises. Furthermore, when the constitution of a Japanese enterprise is taken into consideration, a concrete perspective of the future demand for advanced composite materials must be obtained.

The Japanese CFRP industry was established in a very short period of time under the guidance of Hayashi. However, it cannot be overlooked that, in the process of developing CFRP products and forming the CFRP market, Japan learned a lot from concrete examples already found in the United States.

How to tap the potential market for advanced FRPs is not a problem peculiar to Japan. It is thought that the United States and Europe also must solve the same problem.

Recently, I started making various efforts with the aim of contributing to the expansion of the market for advanced FRPs. I am hopeful that the efforts for market expansion will come to be shared at the international level.

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Heat Resistant Polymer-Matrix Composites Developed

43063802o Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 87-89

[Article by Kuniaki Tobukuro, Polymer Research Laboratories, Toray Industries, Inc.: "Development of Heat Resistant Polymer-Matrix Composites"]

[Text] **Abstract:** Heat-resistant polymers are needed for applications as structural components in advanced aircraft and space vehicles. But the utilization of existing heat-resistant polymers is restricted to some special applications because of processing and mechanical properties problems. Since 1981, easy processable heat resistant polymers had been developed at Research and Development Institute of Metals and Composites for Future Industries as a part of the R&D project of Basic Technology for Future Industries' sponsored by Agency of Industrial Science and Technology, MITI.

The development of easy processable heat resistant polymers have been attempted by three approaches: 1) modification of end-capping agent of nadiimide end-capped PHR polyimide; 2) nadiimide end-capped imide oligomer soluble in common, benign, volatile solvents; 3) addition curable polyphenylquinoxaline oligomer. This paper reports an outline of the progress of easy processable polyimides and polyphenylquinoxaline and their carbon fiber reinforced composites.

1. Introduction

Whereas the advanced epoxy resin-matrix composite materials have steadily been growing as structural materials for use in the aeronautical and space field, the heat resistant polymer-matrix composite materials have not yet come to be used on a significant scale except in some limited areas. This is because there are problems with the existing heat resistant polymers regarding formability and mechanical properties. In the field of advanced aircraft and space vehicles, it is necessary to urgently enhance the performance of heat resistant polymers.

The composite material research work in progress under the Next-Generation Industrial Basic Technology Research and Development System inaugurated in

1981 is aimed at developing easy-to-form, heat resistant matrix polymers. The polymers in the process of development under the R&D project are the following three: 1) new-end capped polyimide resin; 2) new main chain-type polyimide resin; and 3) addition-curable polyphenylquinoxaline resin. Today, representing the material development group, I will report the progress in the development of these new heat resistant matrix resins and discuss the features of composite materials to be produced using the matrix resins.

2. Development of Polyimide-Based Resins

2.1 New End-Capped Polyimide (ANPI)

The PMR-15 and other nadiimide end-capped addition-curable polyimides have high resistance, but molding composite materials containing that type of polymers requires the use of high temperatures and high pressures.¹ With the aim of finding a way to make such polyimides easier to form, we studied the end-capping agents for them. As a result, we found that use of an end-capping agent comprising only an N-allyl-type end group results in slow curing and low heat resistance of the composite and that using allylimide end-capped polyimide to modify nadiimide end-capped polyimide enables the polyimide resin to cure at lower temperature and obtain higher heat resistance than when only the N-allyl-type end group is used. Subsequently, we succeeded in developing an N-allyl end-capped modified polyimide resin. The N-allyl end-capped modified polyimide permits curing reactions to start and make progress at low temperature so that, when the conventional resin forming method is used, it is unable to show adequate fluidity. As a means of giving it higher fluidity in the forming process, we considered the use of a reactive diluent. For the purpose of enhancing the resin fluidity, the diluent must be compatible with the polyimide contents of the resin. Hence we studied allyl compounds having a structure similar to that of the N-allyl-type end-capping agent. Consequently, we have found that using TALC as a diluent is most effective in increasing the fluidity of the polyimide resin and that doing so also results in higher heat resistance of the composite material to be produced using the resin.²

2.2 New Main Chain-Type Polyimide (SEPI)

Among the polyimide resins used for the production of composite materials, the PMR-type polyimide³ is well known. It is produced by prepregging reinforcement fibers with a mixture of monomers and then, for molding, by converting it into an imide and making it undergo a cross-linking, curing process. The existing PMR-type polyimide is effective in improving the tackiness and drapability of the prepreg or in making the resin more fluid in the molding process. However, when it undergoes reactions for conversion into an imide during the molding process, it causes volatile matter such as alcohol or water to be generated. The volatile matter often becomes the source of defects in the molded resin. Moreover, it makes side reactions during the prepregging process or while the prepreg is stored, thereby causing the resin performance to deteriorate.^{4,5} In an attempt to solve the problem, we conducted research to develop an imide oligomer soluble in a solvent whose boiling point is low and succeeded in developing

such an imide oligomer by using 3,3'-EDDM containing an ethyl substituent as the aromatic diamine to constitute the main chain. It has been found that the imide oligomer has a remarkably low melt viscosity and high fluidity, as compared with the polyimide produced by the PMR method in which the polyimide generation is preceded by the acid-component esterification.⁶

3. Addition-Curable Polyquinoxaline-Based Resin (NTPQ)

Research on the composite materials containing, as their matrix, a polyphenylquinoxaline-based resin which is superior to the polyimide resin --a well-known heat resistant matrix resin--in environment resistance (particularly, in water resistance and oxidation resistance) has not advanced very much. The polyphenylquinoxaline resin is difficult to mold. Therefore, to improve the moldability of the polyphenylquinoxaline, we developed 4-nadiimide-0-phenylenediamine as an end-capping agent to be used to turn the polyquinoxaline-based resin into an addition curable resin and subsequently succeeded in developing an addition curable polyquinoxaline resin. We then studied the chemical structure and heat resistance of its main chain and the fluidity of the oligomer and optimized the main chain. Finally, we optimized the mean molecular weight of the oligomer and developed an addition curable polyphenylquinoxaline resin.⁷

4. Properties of Heat Resistant Composite Materials

We produced preregs containing heat resistant matrix resins reinforced with Torayca T400H fibers and evaluated the properties of the composite materials. As the results given in the following table indicate, they showed high heat resistance and good mechanical properties.

Table 1. Composite Properties

| | | | AMPI | SEPI | NTPQ |
|------------------|----------------|-----|-------|-------|-------|
| Heat resistance | T _g | C | 314 | 289 | 317 |
| | T _d | C | 423 | 472 | 505 |
| Tensile strength | RT | MPa | 2,430 | 2,420 | 2,390 |
| | 250°C | MPa | 2,280 | 2,310 | 2,290 |
| Elastic modulus | RT | GPa | 167 | 173 | 170 |
| Elongation | RT | % | 1.4 | 1.4 | 1.4 |
| ILSS | RT | MPa | 135 | 130 | 75 |
| V _f | | % | 67 | 65 | 67 |

5. Conclusion

The development of easy-to-mold heat resistant resin is still in its early stage in which only a basic framework for research has been formed. In the present stage, it is necessary to make efforts toward further improving the

processability and moldability of preregs. At the same time, to promote the development of heat resistant resins, efforts to develop their applications and positively try to use them are also required. In this sense, we count on support and cooperation from various sectors.

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3-D Fabric-Based Composite Materials

43063802p Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 90-92

[Article by Kinji Fukuta, Research Institute for Polymers and Textiles: "Development of 3-D Fabric-Based Composite Materials"]

[Text] **Abstract:** The following results have been obtained from a recent research project on 3-D fabrics and a near-net-shape molding technique:

- 1) The 3-D fabrics have greater loading effects as a reinforcer. In respect of CFRP, their strength and modulus are equal to those of biaxial reinforced materials with comparable fiber volume; specifically these fabrics are found to have unique shearing strength and fracture toughness.
- 2) Also notable is the excellent ablation qualities of composite materials prepared from 3-D fabrics which have such interlacing construction that their roving in varying direction zigzag at intersections with one another.
- 3) A new molding system for 3-D fabrics for long, high-fraction structural elements has been developed which can produce crack-free materials with fiber assemblage well impregnated with resin.
- 4) Based on the braid-making process, the research project has also worked out a mechanism that arranges rovings in multiaxial directions and another mechanism which can make solid-contour endowments.

Use of the 3-D fabrics as a base for composite materials provides those mechanical and thermal properties which can hardly be expected from conventional materials. The molding technique using 3-D fabrics is not liable to involve any of the defects that may result from the cutting or joining process in the conventional method. It is expected that this will combine with desirable qualities of the material to offer favorable multiplier effects.

1. Introduction

A feature of the fiber-reinforced composite materials is that they permit the use of the tailored design technique for optimizing the fiber

configuration according to the product performance requirements. To make full use of this feature, it is necessary to realize practical techniques for producing three-dimensional fabrics (3-D fabrics), whose structures match the fabric orientations and which have required three-dimensional contours, and develop the near-net-shape molding technique needed to integrate 3-D fabrics and matrices.

In this paper, the author will discuss the results of research on 3-D fabrics and the near-net-shape molding technique conducted under the Next-Generation Industrial Basic Technology Research and Development System, focusing on the following topics (organizations in charge of the corresponding research are indicated in parentheses):

- o Conditions for structuring 3-D fabrics and effects of using 3-D fabrics as bases for composites (Research Institute for Polymers and Textiles).
- o Near-net-shape molding technique for 3-D fabrics to be used as structural elements (Mitsubishi Heavy Industries, Ltd.).

In addition, the author will also introduce some of the results of research work done by private enterprises in cooperation with the government in another R&D project with the main aim of developing automatic weaving techniques. The author's intention in doing so is to enable the present trend in composite materials containing 3-D fabrics to be grasped and the future trend to be predicted with higher accuracy and their prospects to be considered based on more integrated information.

2. Structures of 3-D Fabrics

The 3-D fabric research done in the present project has been centered on triaxial 3-D fabric structures. Figures 1 and 2 schematically show different fabric structures. In the orthogonal-array triaxial 3-D structure, rovings intersect one another in a straight fashion. High-density fabrics can be obtained from this structure. In the entangled-array triaxial 3-D structure, rovings are interlaced in a zigzag fashion. This structure can maintain a necessary fabric configuration even at a very low density. Figure 2.2 [as published] shows another type of interlaced structure.

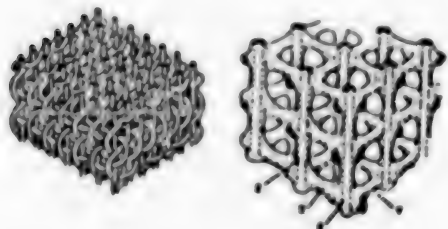


Figure 1. Uninterlaced Structure

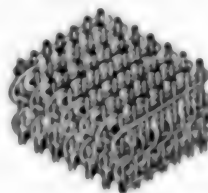


Figure 2. Interlaced Structure

3. Conditions for Structuring 3-D Fabrics and Effects of Using 3-D Fabrics as Bases for Composites

3.1 Mechanical Effects of Combining

The mechanical properties of epoxy composite materials produced using orthogonal-array 3-D fabrics, which are woven of rovings consisting of different numbers of fibers, as the base materials and those of a bidirectionally reinforced composite material produced by laminating plan fabrics made of the same material as described above are compared in Table 1. In Table 2, different samples are compared in terms of fracture toughness. The effects of using 3-D fabrics as the bases for composite materials are great. The values of various kinds of strength and elastic moduli of 3-D fabric-based composite materials are comparable to those of bidirectionally reinforced (laminated) materials of approximately the same fiber filling factor. They have particularly high shearing strength and fracture toughness.

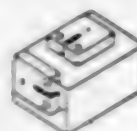
Table 1. Mechanical Properties of 30 Composites (Epoxy/graphite)

| | | 30-1 | 30-2 | L.S |
|-------------------------------|---------|------|------|-------|
| Number of filament | | 3 Kf | 6 Kf | 3 Kf |
| Content | V_f % | 52.6 | 50.4 | 57.1 |
| Specific gravity | | 1.51 | 1.49 | 1.53 |
| Tensile strength | MPa | -- | 746 | -- |
| Tensile modulus | GPa | 61.8 | 56.1 | 62.9 |
| Tensile specific modulus | GPa | 40.9 | 37.7 | 41.1 |
| Flexure strength | MPa | 760 | 673 | 736 |
| Flexure specific strength | MPa | 503 | 452 | 481 |
| Flexure modulus | GPa | 55.3 | 51.1 | 55.7 |
| Flexure specific modulus | GPa | 36.6 | 34.3 | 36.4 |
| Compressive strength | MPa | 477 | 415 | 459 |
| Compressive specific strength | MPa | 316 | 272 | 300 |
| Compressive modulus | GPa | 61.4 | 48.5 | 62.7 |
| Compressive specific modulus | GPa | 40.7 | 32.6 | 41.6 |
| Shearing strength | MPa | >163 | >161 | >42.1 |
| Poisson's ratio | | 0.13 | | |

3D: 30 system, L.S.: laminate system

Table 2. Comparison of Fracture Toughness of 3-D and 2-D Graphite/Epoxy Composites

| Specimen | 3-D | | | 2-D (Laminated) | |
|--|------|------|------|-----------------|------|
| | A | B | C | A | B |
| Maximum load P (kgf) | 357 | 578 | 490 | 557 | 20.5 |
| Fracture toughness KQ (kg/mm ^{3/2}) | 76.7 | 82.8 | 70.8 | 79.2 | 2.9 |



Remark

$$KQ = (P/BW^{1/2}) \cdot f(a/w)$$

$$f(a/w) = (2+a/w) (0.886+4.64a/w-13.32a^2/w^2 + 14.72a^3/w^3 - 5.6a^4/w^4)/(1-a/w)^{3/2}$$

3.2 Ablation Performance

Composite materials based on 3-D fabrics having an interlaced structure in which rovings in various directions are interlaced in a zigzag fashion are expected to show good ablation performance, since surface-layer exfoliation does not easily occur in such a structure. Samples of orthogonal-structure and interlaced-structure 3-D fabrics woven of rovings made of 12,000 carbon fibers each and arranged at the same density were prepared and were molded by impregnating them with phenol resin. The molded samples were then subjected to a burn test in which an oxyacetylene flame was blown out toward each sample and the change caused in the configuration of the sample surface was observed. The results of the burn test are given in Table 3. When an orthogonal-structure sample was exposed to an oxyacetylene flame at a distance of 70 mm, a dent was formed on its surface in 60 seconds, but an interlaced-structure sample tested under the same conditions developed almost no change in its surface in 60 seconds. The surface of the latter sample developed a dent after the test time exceeded 90 seconds, but the area of the dent was smaller than that generated in the former sample. Thus, it is shown that the composite materials based on a 3-D fabric having an interlaced structure show superior ablation performance.

4. Near-Net-Shape Molding Method for Structural 3-D Fabrics

The 3-D fabric composite materials are oriented toward a tailored design concept. A basic target to be achieved in the field of the 3-D fabric composite materials is to establish a near-net-shape molding technique for unifying a 3-D fabric, which has been woven in a shape close to the final shape of the composite material to be produced with the matrix material without destroying the contour of the 3-D fabric. The technique is particularly important from the viewpoint of making 3-D fabrics available with higher density and in more complicated shapes.

Table 3. Burning Test for Ablation

| Shape of sample (mm) | Structure of preform | Burning temperature (°C) | Pressure of gas (PSI) | | Burning distance (mm) | Burning time (sec) | Ablation area (cm ²) | Abl. Depth (mm) | Observation |
|---|--------------------------|--------------------------|-----------------------|-----------|-----------------------|--------------------|----------------------------------|-----------------|----------------------|
| | | | Oxygen | Acetylene | | | | | |
| Rectangular (50 × 100 × 25) | Non-interlaced 3D fabric | 1,000 | 20 | 13 | 160 | 60 | — | — | no change in preform |
| | | | | | 160 | 120 | 3.5 | 3.2 | fiber flay out |
| | | | | | 70 | 120 | 2.0 | 3.8 | formed a hole (3rd) |
| | Interlaced 3D fabric | | | | 160 | 60 | — | — | no change in preform |
| | | | | | 160 | 120 | — | — | no change in preform |
| | | | | | 70 | 120 | 1.1 | 2.6 | formed a hole (1st) |
| Reference Consumption value of gas Oxygen : 1.7 ml/h. Acetylene : 0.94 ml/h. | | | | | | | | | |

We fabricated a resin impregnation and solidification apparatus for impregnating fabrics with a specified amount of resin under a high pressure and used it to determine the basic conditions for molding 3-D fabrics into near-net shapes. The curves plotted based on the data obtained using the system are shown in Figures 3 and 4. The molding tests were conducted in 3-D fabrics having a rectangular section and those having an I-shaped section at a temperature of 393 K (120°C) and under a pressure of 784 KPa (8 kgf). Under these conditions, a lower resin viscosity and a higher resin impregnation speed can be expected. A photo of the resin impregnation apparatus is shown in Figure 5 [not reproduced]. Based on the data on the basic conditions for molding obtained through the test, we additionally adopted a latter pressurization process (12,544 KPa), improved the resin composition (resulting in an 8.4-percent increase in breaking elongation), and enhanced the uniformity of fabric density.

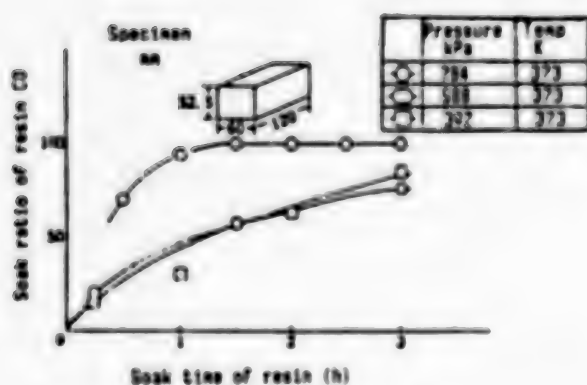


Figure 3. Soaking Ratio/Temperature Curve of Resin Impregnation Process

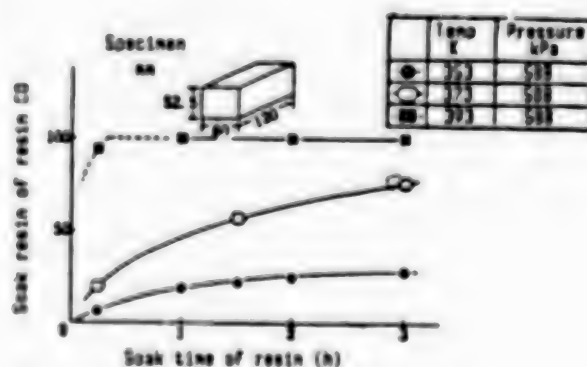


Figure 4. Soaking Ratio/Time Curve of Resin Impregnation Process

Through such improvements, we eventually succeeded in making it possible to mold long, high-density structural 3-D fabrics (having an I-shaped section, a Vf value of 50 percent and a 1-m length) allowing them to be adequately impregnated with resin without causing them to crack.

5. Automatic 3-D Fabric Weaving

A system for weaving 3-D fabrics requires a function for arranging rovings in multiaxial directions and another for fabric contouring. A photo of an apparatus which, having such fundamental functions for fabric weaving, basically performs a 3-D braid-making process is shown in Figure 6 [not reproduced]. To make 3-D fabrics available as industrial materials, it is essential to develop automated high-productivity looms. A photo of the main part of a fully automatic loom for 3-D fabrics developed in the foregoing joint research work project is shown in Figure 7 [not reproduced]. The loom is capable of automatically weaving triaxial 3-D fabrics ranging from low to high in density without damaging rovings.

6. Conclusion

Using 3-D fabrics as bases for composite materials makes it possible to produce composite materials having mechanical and thermal properties that can hardly be expected from the conventional materials. The new technique for weaving 3-D fabrics and molding them into shapes matching those of the structural elements or products to be produced using them does not involve the risk of defects that may result from the conventional cutting or joining process and, therefore, will enable the production of higher-reliability composite materials. It is expected that the enhanced composite material reliability combined with the desirable material properties achieved using the new technique will produce great multiplier effects. Thus, the fruits of the present research work, even though many problems are yet to be solved before they can be put to practical use, will contribute toward establishing the composite material techniques oriented toward near-net-shape molding.

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Advanced Fabrication Technologies for Polymer-Matrix Composite Materials

43063802q Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 93-95

[Article by Hoshiaki Sakatani, Mitsubishi Heavy Industries, Ltd.: "Development of Fabrication Process for Polymer-Matrix Composite Materials"]

[Text] **Abstract:** Although the fabrication technology for advanced polymer matrix composite materials is based on that for conventional glass fiber reinforced plastics (GFRP), the idea that the fabrication process is the key technology for composite materials is being accepted. This paper presents advanced fabrication technologies of polymer matrix composite materials for structural applications which have been developed extensively by the contract researchers of the R&D Institute of Metals and Composites for Future Industries, covering the following items:

- Continuous bend-forming process
- Heat transfer fluid method
- Microwave heating process
- Aligned-whisker interlaminar reinforcing process.

1. Introduction

The composite materials have been developed to such an extent that any structural design division, where the concepts of new products are worked out, of any enterprise cannot afford to manage without using any composite material. In such a situation, the importance of the composite material forming techniques, which constitute the key to the practical applications of composite materials, has been well recognized by the industrialized countries and they have been engaged in fierce competition to develop the techniques. There may be an infinite number of ways in which composite materials composed of fibers and a shape-determining matrix resin can be produced and formed, i.e., fabricated. This paper will generally discuss the results so far obtained of the research work for the development of new composite material forming techniques being conducted under the Next-Generation Industrial Basic Technology Research and Development System and the areas where the new techniques can be utilized.

The new forming process uses a system consisting of, as shown in Figure 2.2.1, 1) a pressurization section; 2) a heating or cooling section; 3) a liquid transfer section; and 4) a forming section.

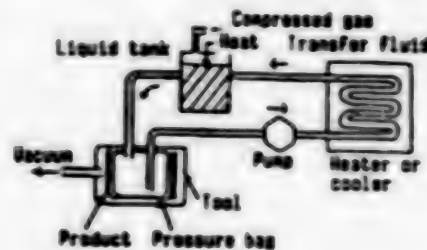


Figure 2.2.1 Composite Manufacturing Method by Heat Transfer Fluid

The features of this forming process include: 1) this process can be used without being restricted by the product size and 2) since this process uses a liquid as a hot pressure-medium which has high heat conductivity and can be fed to only the locations where it is needed, it is more energy-economical than the conventional autoclave process.

Hollow circular cylinder samples with hat stringer reinforcements were produced by the new process using a CF-epoxy prepreg. The produced samples were equivalent both in terms of quality and forming accuracy to those produced by the autoclave forming process.

Since the temperature and pressure can be controlled with ease for the new process, the new process has great potential for application to the fabrication of large products made of heat resistant, thermosetting resin or thermoplastic resin, the forming conditions of which are difficult to control.

2.3 Microwave Forming Process (Under development by Fuji Heavy Industries, Ltd.)

Microwave heating has many advantages, but, with not much data on its applications available, it has been applied only in limited areas. In the present research program, studies have been made for the development of a polymer matrix composite forming process in which microwave heating is used. Through the studies, it has been found that microwave heating can be used to cure polymer matrix composite materials, even though its heating characteristic is affected by the electric properties of the reinforcement fibers such as the Kevlar fabric (nonconductor), silicon carbide fiber (semiconductor), and carbon fiber (conductor) (Figure 2.3.1). Furthermore, through composite forming tests conducted using wave-transmissive molds, it has been found that varied types of polymer matrix composite materials reinforced by different types of fibers can be cured by microwave heating. However, the tests also revealed that it is difficult to uniformly heat different sizes and shapes of samples and therefore that microwave heating as it is not appropriate for fabricating large composite material parts. At present, research for the development of a method of uniform heating is

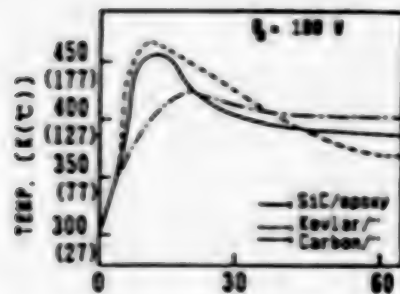


Figure 2.3.1 Microwave Heating Properties

being conducted using wave-absorptive molds which can be quickly heated by microwaves.

It is thought that microwave heating suitable for quickly heating composite materials will be usable for continuous composite forming or composite forming in special environments (for example, in space). It can also be used in combination with the conventional electric heating to make more effective heating. With these features, microwave heating is expected to be applicable to new polymer matrix composite materials that must be processed at high temperatures.

2.4 Laminar Composite Reinforcement by Whisker Dispersion (Being researched by Mitsubishi Electric Corp.)

Laminar composite materials are widely used, as they can be given inplane properties widely ranging in value and they are easy to fabricate. However, since they are not reinforced in the antiplane directions, their strength against interlaminar shear or tension in the direction of their thickness is small. Therefore, it used to be inappropriate to produce thick or complicated-shaped parts made of laminar composite materials. The possible means of eliminating the weak point of the laminar composite materials include the use of three-dimensional fabrics and stitching. In the present research work, however, laminar composite-material reinforcement by means of dispersing whisker fibers, as schematically illustrated in Figure 2.4.1, is being studied from the viewpoint of retaining their features, being produced with high productivity and easily formable.

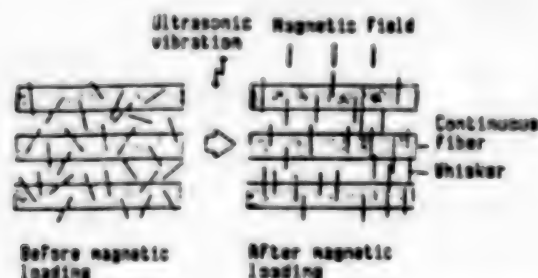


Figure 2.4.1 Concept of Interlaminar Reinforcement by the Dispersion of Whiskers in the Matrix

What should be given attention in the theory, illustrated in Figure 2.4.1, of laminar composite reinforcement by whisker dispersion is the use of a magnetic field to control the whisker orientation. For the purpose of materializing the control of whisker orientation by means of a magnetic field, a technique for thinly plating whisker fibers with ferromagnetic material has been developed. It has already been confirmed that whisker fibers plated with ferromagnetic material can be controlled using a magnetic field and that the whisker orientation control can be made easier by also applying ultrasonic waves. At present, laminar-composite forming experiments are being carried out using a magnetic field press for the purpose of verifying the theory illustrated in Figure 2.4.1.

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Material Design of Bioelectronic, Molecular Electronic Devices

43063803a Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 97-99

[Article by Masuo Aizawa, Department of Bioengineering, Tokyo Institute of Technology]

[Text] **Abstract:** International conferences on bioelectronic and molecular electronic devices are chronologically described in relation with the Japanese national projects by MITI. The current status of research on bioelectronics and molecular electronics has been reviewed with four topics: 1) molecular assembling technologies; design of molecular interface; 2) design of bioelectronic sensors; 3) design of neurodevices; and 4) design of biocomputers.

1. Introduction

F.L. Cater of the U.S. Navy NRL lectured on the concept of molecular electronic devices in 1979 and sponsored the NRL Workshop on molecular electronic devices three times (1981, 1982, and 1986). McAlear of the U.S. Centronix Co. outlined the conception of bioelectronic devices and biochips and promoted the social concern regarding bioelectronic devices. In November 1985, the International Symposium on Bioelectronic Devices and Molecular Electronic Devices was held in Tokyo and the research conditions and future courses on bioelectronic devices were outlined. After that, the project on "Bioelectronic Devices" was started in 1986 by the Agency of Industrial Science and Technology of MITI as a link in its Basic Technology for Future Industries Project; "bioelectronic devices" came to be taken up as an international frontier project of the Science and Technology Agency; and a setup for research cooperation among the industrial, governmental, and academic circles centered around Japan came to be prepared. Among the research on bioelectronic devices, that on biosensors has encountered new research conditions and the blending of biology and electronics has accelerated. Progress on organic thin films and especially the Langmuir-Blodgett (LB) membrane and on bioengineering is attracting attention as the basic technologies for research on bioelectronic devices. Moreover, conditions have also ripened for trying to produce a new information processing system like that of the cerebral and nervous systems as the model, and the approach towards a biocomputer and neurocomputer has also become active.

2. Bioelectronic Device Construction Technology: Design of Molecular Interface

Many problems must be solved to realize a new functional device by utilizing biomolecules. The electron transfer of the protein molecule is controlled very cleverly in a living body. The molecular construction, etc., in a photosynthetic reaction center of bacteriochlorophyll clearly indicates the construction of such an electron transfer in a living body. Research has progressed on trying to control the molecular array of the biomolecule and realizing an effective electron transfer.

The LB membrane was applied for control of the protein molecular array. The bacteriorhodopsin which constructs a purple membrane of the high-degree halophilic bacteria is an experimental material suited for LB membrane preparation. The bacteriorhodopsin is extracted from the purple membrane, an LB layer of either the monomolecular layer or the multimolecular layer is prepared, and the regularity of its construction, etc., are studied in detail. The relationship between the photoelectric conversion function and the molecular array control has been clarified on the molecular membrane of the bacteriorhodopsin and there are expectations that a design guideline may be available on the construction of bioelectronic devices.

Cytochrome is an important electron transfer material in a living body and its construction has also been clarified recently. Since the LB membrane could not be formed by the cytochrome C independently, about 10 layers of barium stearate monomolecular layers were laminated by the LB membrane of the barium stearate and cytochrome C was made to adsorb and become fixed on top. The molecular orientation condition of the adsorption cytochrome C was clarified by means of the polarization fluorescence method. The purpose of realizing the molecular orientation control of cytochrome C lies in preparing a bioelectronic device by assembling several types of proteins.

The protein capable of performing a smooth electron transfer with the electrode was cytochrome C only. However, it has now come to be expected that the electron transfer of many biomolecules will be realized by utilizing the molecular interface of the electron promoter, etc., besides the electron mediator.

The electron transfer of protein has also been realized by utilizing the electroconductive polymer as the molecular wire. When a controlled potential oxidation is made after inserting the electrode into an aqueous solution containing pyrrole and enzyme molecule (for example, a glucose oxidase), a polypyrrole thin membrane embracing the enzyme molecule is formed on the electrode surface. It has been made clear that the embraced enzyme molecule maintains the enzyme function and that it is an electroconductive enzyme membrane capable of performing the electron transfer between the enzyme molecule and polypyrrole. This electroconductive enzyme membrane is considered an extremely effective method as it can be formed directly on a metal or a semiconductor electrode surface and the membrane thickness is controlled by the quantity of electric current passed.

A more important phenomenon has been discovered on the electroconductive enzyme membrane. This is the fact that the enzymatic activity of the electroconductive enzyme membrane changes considerably by relying on the electric potential. This means that the electric control of the enzymatic activity has been realized.

3. Bioelectronic Sensor

Research on the biosensor utilizing the molecular recognition ability of the biological substances has shown remarkable development and the blending with electronics such as the introduction of semiconductor process technology has been conspicuous in recent years. The most actively promoted research is that on the enzyme FET (ENFET) which has formed an enzyme thin membrane in the gate of the ion sensitive field-effect transistor (ISFET). The molecular recognition is difficult in a semiconductor material. Molecular recognition has been realized by blending the semiconductor material and the biological substance. However, the development of a preparation method for the enzyme thin membrane adapting to the wafer planar process is the problem. We have recently developed an electrochemical application of the microbiosensor.

Research on immunosensors utilizing the molecular recognition function of the antibody molecule has also progressed. It has been recognized that the surface acoustic wave and the surface plasmon change when the antigen bonds with the antibody thin membrane formed on the surface of the surface acoustic wave (SAW) device and the metal thin membrane, and there has been an attempt to apply these to the immunosensor.

With the development of the bioelectric sensor, forming a molecular membrane that has array controlled the biological molecule has become an important problem. The enzyme molecule was adsorption fixed to the LB membrane of the fatty acid and was applied to ENFET. There is very little evidence that the characteristics of ENFET are affected by the molecular orientation of the enzyme, but the molecular array control of the antibody is extremely important in the design of the immunosensor.

4. Approach to Neurodevices

The realization of a neurodevice with a synapse function which is the pivot of the nerve network also has a bearing on the path to a biocomputer and it is an important theme. Several variations have been seen in the approach to neurodevices.

The first approach is the realization of a molecular communication system utilizing information molecules such as the neurotransmitter. We have prepared a device capable of simulating the synapse front membrane function by using graphite, polyacethylene or polypyrrole film. The neurotransmitters such as the acetylcholine and glutamic acid are electrically stored in this device and releasing the neurotransmitters has become possible by applying a microvoltage pulse. The second approach is concerned with the synapse back membrane and a lipid membrane accompanying

an oscillation phenomenon has been suggested. Yoshikawa and his group have impregnated an α -monooleate (monoolein) in the porous membrane made of Teflon (bore size 10 μm) and have recognized an automatic oscillation phenomenon. The artificial synapse has been prepared under the abovementioned approaches and molecular communication will be realized outside of a living body.

5. Biocomputer

There are several paths in the research on trying to make a biocomputer with bioelectronic devices like the neurodevice. Conrad has suggested the double dynamics device. This is a device that utilizes the two-stage dynamics system. Hopfield has replaced the nerve network with an analog circuit and has indicated the possibility of making it into hardware. After this, a movement to prepare an engineering model (neuro net) of the nerve network has rapidly progressed centered around the United States.

Table 1. International Conferences on Bioelectronic and Molecular Electronic Devices

| | |
|------|--|
| 1979 | NRL Seminar on Electroactive Polymers (Washington, D.C.) |
| 1981 | NRL Workshop on Molecular Electronic Devices (Washington, D.C.) |
| 1982 | STR Symposium on Bioelectronics (Zurich) |
| 1983 | Gordon Research Conference on Organic Thin Films First International Conference on LB Films (Durham) Second NRL Conference on Molecular Electronic Devices |
| 1985 | Second International Conference on LB Films (Shenectady, N.Y.) International Symposium on Bioelectronic and Molecular Electronic Devices (Tokyo) |
| 1986 | Gordon Research Conference on Organic Thin Films Third NRL Workshop on Molecular Electronic Devices |
| 1987 | International Symposium on Molecular Electronics and Biocomputers (Budapest) |

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Synthetic Bilayer Membranes as Self-Organizing Materials

43063803b Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 100-102

[Article by Toyoki Kunitake, Faculty of Engineering, Kyushu University]

[Text] **Abstract:** Bilayer membranes formed from a large variety of synthetic amphiphiles belong to an important class of self-organizing material. Facile molecular design based on the module concept and the rich variety of the component structure render synthetic bilayers a highly attractive candidate of the future organic material. The two-dimensional molecular array in the bilayer gives rise to new magnetic and electronic properties. Regular multilayer films are obtainable by casting aqueous bilayer dispersions. The synthetic amphiphiles are also suitable for preparing surface monolayers and the Langmuir-Blodgett film. [End abstract]

The characteristics of materials such as metals and polymers have a close relationship with the peculiar system structure which the respective materials have. Living things such as animals and plants have a precise system structure that has no comparison with metals and polymers and this precise system structure makes possible high-degree functions. When seen from the minuteness of the system structure, the system of animal and plant bodies are structured at a far finer molecular level as the standard unit than that of metals and polymers which are constructed of a precise system of the phase level such as the crystal and amorphous. Therefore, it is necessary to aim at a system structure of the precise molecular level of organisms for turning out functions close to that of organisms with artificial materials.

Now, let us consider what sort of measures can be considered in order to achieve this goal. For systemizing the "atom" which is the smallest unit of materials, a means called superlattice which is made by stacking up these atoms one by one has been developed. However, the greatest significance lies in the combination made by effectively utilizing the complicated shapes which the individual molecules have when systemizing the "molecules." The systemization method of the atom cannot be applied as it is.

The precise molecular system which animals and plants have become a single functional unit as the proteins and lipids that are the basic materials spontaneously become compounded and the precise molecular system is made up by this functional unit growing into more complicated cells and organs. When starting from a material having such a "self-organizing property," it may be possible to turn out a system having a molecular level preciseness close to organisms also in artificial materials. The protein molecule has a three-dimensional structure which the linear polymer (peptide) produces by being precisely folded. However, designing this structure freely and using it as an artificial material still remains for the future. In contrast, the bimolecular membrane is an orderly structure produced by the lipid molecules gathering two-dimensionally and it is relatively easy to reproduce this with an artificial material.¹ Kunitake and Okabatake in 1977 discovered that the two-chain type ammonium salt of a simple molecular structure indicated a similar self-organizing property as the biolipid and that it spontaneously became a bimolecular membrane endoplasmic reticulum in water.² After this, several hundreds of types of membrane material molecules have been synthesized by domestic and overseas research groups, and the synthetic bimolecular membranes formed by these membrane material molecules have come to take a position as a new field in chemistry.

The ease of the molecular design and the richness of the types of membrane materials are the outstanding characteristics of the synthetic bimolecular membrane and it is an extremely promising self-organizing property material. The representative type diagram of the bimolecular membrane is shown in Figure 1. The membrane material is made from the combination of several partial structures (modules) and when taking the two-chain type compound similar to the biolipid as an example, it consists of four types of partial structures such as the hydrophilic head and hydrophobic tail. The head part plays the key role in the stability of the membrane interface and the tail part plays the key role in the molecular orientation in the membrane.



Figure 1. Representative Corresponding Bilayer Structures

An example of the characteristic generated from the two-dimensional self-systemization is observed in a metal complex membrane.³ The single chain type compound having a cyclic polyamine as the hydrophilic group produces a stable complex with transition metals such as Cu^{2+} , and the produced complex becomes a bimolecular membrane when dispersed in water. The copper ions in the membrane mutually indicate a very great antiferromagnetic interaction not seen in ordinary copper (II) complex. It can be concluded that the

synthetic bimolecular membrane is an effective system also in the systemization of the electron spin through the systemization of molecules. Moreover, the azobenzene group is systematically aligned two-dimensionally in the bimolecular membrane containing the azobenzene group. A new photochemical effect not seen in isolated chromophore is produced by the array of the chromophore having such a π -electron. For example, there is the fact that the energy of light moves with good efficiency in the membrane.

Forming the bimolecular membrane is the self-systemization in the molecular level and this can be further expanded at the macroscopic level.⁴ When the bimolecular membrane water dispersion liquid is spread on a glass plate and slowly dried, a transparent membrane remains. This membrane can be peeled off from the glass plate and held in one's hand. It is clear from the X-ray structure analysis report that the layers of the bimolecular membrane are stacked in parallel to the film surface. Various new possibilities are opened when utilizing this macroscopic self-organizing structure. For example, the molecular orientation complying with the charge distribution on the complex molecules can be controlled when the plane type copper complex is integrated as the counter ion of the hydrophilic part. Moreover, the cast membrane of the fluorocarbon type membrane has the characteristic as an oxygen enrichment membrane.

The molecule becoming the material of the bimolecular membrane is also superior as the water surface monomolecular membrane material. Although there have been systematic investigations on the monomolecular membrane formation, there is no difference between the basic molecular orientation structure and the dispersed bimolecular membrane. Moreover, the LB membrane is also available by transcribing it on a solid substrate.

As mentioned above, the bimolecular membrane material is a molecular material rich in the self-organizing property and various precision molecular membranes can be produced by starting from here. It is believed that its utilization will increase in the future.

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20158/9365

Organic Nonlinear Optical Materials

43063803c Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 103-105

[Article by Seizo Miyata, Faculty of Technology, Tokyo University of Agriculture and Technology]

[Text] **Abstract:** In recent years there has been a growing interest in studies of nonlinear optical properties because of the potential application in optical devices. Organic compounds, by virtue of some of their specific properties (electronic, delocalization, charge transfer effects, high polarizability), are particularly suitable for the optimization of physical multiphoton effects associated with the nonlinear interactions of laser beams. However low molecular organic compounds have some demerits because it is technically difficult to grow large size single crystals and to handle mechanically weak crystals. In order to overcome those problems, a new method of adding a guest compound having a large nonlinear optical constant in host polymers and applying an electrical or magnetic field for orientation of active molecules has been tried.

We found recently very strong second order nonlinear optical properties in the guest-host system prepared by crystallization of p-nitroaniline and polyoxyethylene mixture under electrical field.

In this system, p-nitroaniline and polyoxyethylene are used as guest and host molecules, respectively, and form a new crystalline complex. When both components are mixed in the ratio of 1 to 6, and applied by a DC electric field of 20,000 V/cm, the system shows 91 times larger optical second harmonic generation than that of urea. This is the largest among guest-host systems ever reported.

1. Introduction

In reviewing the outlook for the coming 21st century, it can be seen that the quantity and quality of information will rapidly increase and it will become extremely difficult to cope with this trend under the conventional system. The technology that can overcome such a condition and become the basic technology of the next generation is optoelectronics. It is no exaggeration to say that the new materials having photoelectrode functions

support this technology. Since the nonlinear optical material among these new materials converts the wavelength of the laser beam to 1/2 (HG) and 1/3 (THG) and possesses wavelength conversion functions such as the optical parametric oscillation effect of obtaining multiphoton from a photon, etc., and electrooptical functions such as the Pockels effect and Kerr effect, hope is placed in it as an optical pickup, optical guide device, optical bistability device, optical IC, etc., and it is considered to play the central role in optical technologies.

Inorganic ferroelectric materials had been conventionally used, but since an important function was discovered recently on organic substances, it has come to attract great attention. The switching time of the former material was of the pSEC order, whereas the switching time of the latter was of the fSEC order and it indicated a high-speed responding capability. Therefore, it is expected to be used in the optical computer theoretical device. This article will give an outline on the organic nonlinear optical materials centered around our research results.

2. Nonlinear Optical Material Effects of Organic Substances

The nonlinear optical effect is shown by polarization (P) generated by the electric field (E) of light. In other words, it becomes:

$$P = X^{(1)} E + X^{(2)} E \cdot E + X^{(3)} E \cdot E \cdot E + \dots \quad (1)$$

Terms above $X^{(2)}$ indicate the nonlinearity. It becomes $X^{(2n)} = 0$ in substances having a central symmetry crystal structure and a secondary nonlinear optical effect is not manifested.

Since equation (1) above shows the relationship between the macroscopic polarization and the electric field, the microscopic polarization and E relationship is shown in the following equation:

$$P = \alpha E + \beta E \cdot E + \gamma E \cdot E \cdot E + \dots \quad (2)$$

Whereas, α , β , and γ are the molecular susceptibility. The relationship with the macroscopic susceptibility becomes:

$$X^{(1)} = \alpha L_1 N, X^{(2)} = \beta L_2 N, X^{(3)} = \gamma L_3 N \quad (3)$$

Whereas, N = molecular density, L_i = local electric field factor, it becomes, when using the Lorentz approximation:

$$L_i = ((n^2 + 2)/3)^{i+1} \quad (4)$$

On the other hand, the molecular susceptibility is shown as follows according to the quantum mechanical perturbation theory that uses the second level model in the incident light range in which the wavelength dispersion can be ignored:



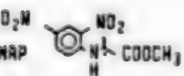
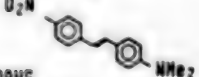
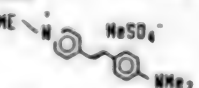
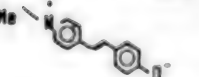
$$\alpha = |\mu_{eq}|^2/E_{eq}, \quad \beta = |\mu_{eq}|^2 \Delta\mu_{eq}/(E_{eq})^2,$$

$$\gamma = (|\mu_{eq}|^2 (\Delta\mu_{eq})^2 - |\mu_{eq}|^4)/(E_{eq})^3 \quad (5)$$

Whereas, μ_{eq} = transition moment, $\Delta\mu_{eq}$ = dipole moment difference of excited state and ground state, and E_{eq} = band gap. It is known from these equations that it is necessary that the equipment and $\Delta\mu_{eq}$ are great and E_{eq} is small for molecules with a large susceptibility. However, the absorption of light shifts to the longer wavelength side and the transparent range becomes narrow when E_{eq} becomes too small.

Organic chemistry techniques have advanced in recent years and it has become possible to control quite freely the dipole efficiency, atomic groups with a large polarizability, conjugate system, and symmetry of molecules. As a result, many organic substances have been synthesized and studied. Table 1 indicates the SHG activity of the representative organic substance, the strength, absorption edge, and β value of the relative 0.53 μ light when urea has been made 1 by using the Nb YAG laser 1.06 μ .¹ There are substances that do not indicate SHG even when the β value is great. This is because the crystal structure has a symmetry. It is necessary to also control the assembly state of the molecules and not only the molecular structure to obtain substances that indicate a large SHG activity. Moreover, it becomes extremely important to provide various properties such as workability, strength, transparency, when using these substances as the material. The hybridization of polymers with superior material characteristics and the hybridization of low molecules with a large β value are under investigation from such a standpoint.

Table 1. Organic Substances Showing Clear Nonlinearity

| Molecular structure | Relative strength for secondary high frequency urea | Absorption edge /nm | β ($\times 10^{-14}$ esu) |
|---|---|-------------------------------------|----------------------------------|
|  | 1.0 [$\times 2.5$] | 200 | 0.45 |
|  | 22 [$\times 3.5$] | 480 | 42 |
|  | 10 [$\times 6.7$] | 500 | 220 |
|  | 0.0 | 430(λ_{max}) ~580 | 450 |
|  | ~250 | 473(λ_{max}) 588(MeOH) | — |
|  | 0.0 | 570(λ_{max}) ~550 | 1,000 |

3. Nonlinear Optical Effect of the Guest-Host System

When p-nitroaniline (P-NA) not indicating an SHG activity was mixed with polyoxyethylene (POE), we found that P-NA and POE formed a complex and discovered that it indicated an SHG activity when crystallized under voltage.

The relationship between the mole ratio of POE and P-NA and the SHG strength is shown in Figure 1. It reaches maximum when the mole ratio is 6:1, reaching 91 times that of urea and 2.6 times that of MNA. It has been confirmed by X-ray diffraction that a new crystal structure without a center symmetry has been formed in this mole ratio. It is also known that it will do to just apply DC voltage of only 100 V against the sample pressure of 0.5 mm in this case. This is the first time in which the polymer has been subjected to hybridization with a low molecular compound, the crystallized state has been controlled, and a large SHG characteristic has been provided.

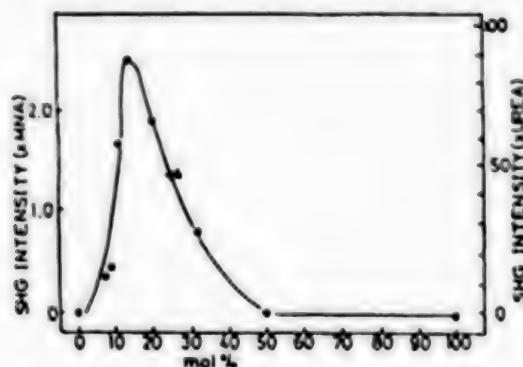


Figure 1. Relationship Between Mole Ratio of POE and P-NA and the SHG Strength

Table 2. Predicted Nonlinear Constant in Polymeric-Organic Dispersion System

| | $\chi^{(2)}$ crystal (cgseu) | $\chi^{(2)}$ predicted (cgseu) (20vix in Polymer) |
|-----|-------------------------------|--|
| | 0 | 2.1×10^{-7} |
| | $d_{11} \ 3.8 \times 10^{-7}$ | 2.3×10^{-7} |
| | 0 | 6.0×10^{-7} |
| | 0 | 1.3×10^{-6} |
| | 0 | 5.0×10^{-6} |
| | $d_{22} \ 3.2 \times 10^{-6}$ | 5.0×10^{-6} |
| POE | $d_{33} \ 1.1 \times 10^{-6}$ | — |

Table 2 indicates the $X^{(2)}$ predicted values and macro $X^{(2)}$ values (actual measured values) calculated by using equations (2) and (3) when the respective functional low molecules are mixed by 20 percent in the polymer and assuming that the orientation is perfect. The interaction between the polymer and low molecules has not been considered at all in the calculation and it has been supposed that the polymer is simply functioning as a matrix. Nevertheless, it has reached 2.6 times that of MNA in case of the POE and P-NA systems and it has become necessary to study in detail the interaction and crystal structure of the polymer and low molecules. Moreover, it is considered that the workability, mechanical characteristics, etc., will improve and applications will be further expanded by mixing it with polymer.

Research is energetically being carried out mainly on polydiacetylene and its derivatives on the third nonlinear optical effect. However, further explanation will be omitted here.

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Laser Annealing, Ablation, Spectroscopy

43063803d Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 106-108

[Article by Hiroshi Masuhara, Kyoto Institute of Technology]

[Text] **Abstract:** Developments in lasers have opened new fields of photofunction, laser processing, and dynamic characterization of organic materials. Molecular approach is indispensable for their basic studies and will contribute to future technologies. From this viewpoint, we have studied the following two subjects in our laboratory. One is to analyze laser annealing and ablation phenomena as photophysical and photochemical processes, using aromatic molecular systems. Another is to develop time-resolved reflection spectroscopic techniques which make it possible to measure molecular motions, excited state dynamics, chemical reactions directly in nanosecond and picosecond time regions. Some of our recent studies are summarized.

1. Introduction

Research on new materials using organic compounds has become active. Especially with the increased application of the laser, developments on photofunction design, laser processing technology, and characterization method using lasers are attracting attention. Understanding the organic molecular electron state in a solid is indispensable in photofunction design and it can be considered that the theoretical research on molecules from the photochemical standpoint is giving birth to the following technologies in the laser process. However, clarifying the functional manifestation mechanism and reaction mechanism remains a problem for the future. First of all the development of the dynamic characterization method has also become a matter requiring immediate attention. We have started research aimed at the aromatic system organic solids for the purpose of solving these problems and we wish to hereby introduce the current state of this research.

2. Laser Annealing of Organic Thin Films¹

The fluorescence spectrum changes when excimer laser is irradiated on the cast film, LB film, and vapor deposition film of the long chain carboxylic

acid containing a pyrene ring. Seen through an optical microscope, it can be considered that the homogeneity of the films has increased by laser beam irradiation and the spectrum change is caused by optical annealing. Therefore, it becomes possible to study the laser annealing phenomenon with fluorescence as the probe. This type of research is also linked to clarifying the annealing mechanism at the molecule and electron levels.

3. Laser Ablation of Polymer Films²

The groups conventionally reported are of polyimide, poly(methyl methacrylate), poly(ethylene terephthalate), and several types of photoresists. All of them possess the carbonyl group, amino group, or contain the hetero atom. From the photochemical standpoint, it means that the luminescence lifetime is short, the cross-yield rate in the triplet state is great, the photochemical reaction is great. This means that the radical reaction occurs easily. On the other hand, although there has been great progress in research on the energy transfer of the polymer system including the π -electron system, excimer generation, and electron transfer, information on the ablation phenomenon is not available. We consider that the latter system is necessary for understanding the ablation phenomenon from the basic photophysical and photochemical levels and have been conducting research by directing our attention to the electron structure of the excited state, chemical and spectroscopic properties of additives and the effects of their concentration which play an important role in ablation.

4. Dynamic Characterization by Reflection Spectroscopy

Spectroscopy generally covers the emission, absorption, scattering, and reflection phenomena and there has been outstanding progress in realizing a high resolution, high precision, and high sensitivity with the introduction of the laser. Another change is the improvement of the time resolution. This provides a perturbation to an object by the pulse laser excitation and measures the ever-changing spectrum by making the change after that as a function of time. The direct measurement of the electron processes such as the molecular motion like the dispersion and conformation change, electron transfer, and energy transfer, the direct observation of the excited state and reaction intermediate, and the elucidation of the reaction mechanism have been made possible and an analysis using the difference of the time constant is also possible. Although the emission, absorption and scattering spectral diffraction have already reached the picosecond order, those of the reflection spectral diffraction are low. On the other hand, when looking at the natural world in general, substances are generally opaque, their absorption and scattering measurements often difficult, and there is no way we can conduct research unless they are radioactive. Therefore, if the time constant of the reflection spectral diffraction can be improved up to the picosecond level, the photophysical and photochemical properties of materials and especially those of the organic solid system may become a quality comparable to that of the gas and liquid phases and it can be considered that there will be a great far-reaching effect. The reflection phenomenon, itself can be further classified into specular

reflection, total reflection, and diffuse reflection. We are now engaged in research on the latter two.

4.1 Diffuse reflection laser photolysis method²

The measurement of the transient UV absorption spectrum is effective for directly pursuing the electron process and the reaction of the light-scattering system. This is obtained by the time change of the diffuse reaction strength of various wavelengths caused by laser irradiation. The hardware and software of the system controlled and processed by a microcomputer were developed and studies were made on various measuring conditions. Reports will be made on the photodynamics of the organic polycrystal, absorption and inclusion systems as application examples.

4.2 Total reflection fluorescence spectroscopy⁴

Generally, when light enters from a substance with a large refractive index to a substance with a small refractive index, the light is totally reflected when the incident angle is greater than the critical angle. The light in this case is infiltrated in the substance with the smaller refractive index as an evanescent wave and it is excited when fluorescent molecules exist in this area. In other words, information on the structure can be obtained in the area of the surface and interface by analyzing the fluorescence emitted only from the area of the solid surface and interface. The permeation depth depends on the substrate and substance combination, wavelength, and incident angle of the excited light. Actually, it will do to measure the dependency on the incident angle of the fluorescence spectrum and fluorescence generating attenuation curve. The depth direction profile for an organic solid can be expected by analyzing these results. Together with preparing a model bilayer membrane and conducting demonstration experiments to improve the time resolution of the total reflection fluorescence spectrometry and indicating its usefulness, studies have been made on the problem points and application ranges of this methodology and it has been established as a new method. In comparison to the ATR IR method and various electron spectroscopies that are frequently used to obtain information on the interface and surface, this method has the following characteristics:

- (1) The depth range of about $0.1\ \mu$ is the goal. The depth of $0.01\ \mu\text{m}$ is also permissible according to experiment conditions.
- (2) It has a high time resolution in the picosecond order.
- (3) Direct knowledge on the electron state and electron process is provided.
- (4) It is not a measurement under vacuum.
- (5) It is a nondestructive analysis.
- (6) Detection of microcomponents is possible.

Measurements on various organic thin membranes and related samples have been made as its application examples and among these measurements, information is obtained regarding the depth aspect on the organic three-layered vacuum deposition membrane, distribution of pigment in silk and polymer film that has doped the π -electron compound.

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Fe-Mg, Mn-Sb, V-Ag Superlattices Described

43063803e Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 109-111

[Article by Teruya Shinjo, Institute for Chemical Research, Kyoto University]

[Text] **Abstract:** Multilayered metal films with artificial superstructures (metallic superlattices) are prepared by alternate deposition of two elements in ultrahigh vacuum. Artificial superlattices are new materials which do not exist in nature and on the other hand are very useful as model systems for fundamental studies. Methods of preparation and structural characterization are described and several examples are introduced. Ferromagnetic monolayers are obtained by combining Fe and Mg and also Mn and Sb. Dimensionality of superconductivity is studied from V-Ag multilayers.

1. Introduction

"Artificial superlattices" are the multilayer films that have controlled the structure at the atom level. A multilayer film regulating the cycle at the angstrom unit has been prepared by using the dual alternate vacuum deposition device shown in Figure 1. The structure in the perpendicular direction of the film can now be artificially designed freely (although unidimensionally). The following are major categories under which the research on multilayer films has been conducted.

- (1) X-ray spectroscopic devices
- (2) Starting substances for solid phase reaction research
- (3) Research on magnetism of interface and two-dimensional layer
- (4) Research on two-dimensional superconductivity
- (5) Research on abnormal modulus of elasticity and multilayer films

Research on the abovementioned (1) and (2) have long been carried out and in comparison to (3) and (4), it is necessary to make the artificial period extremely short. The research that we are now conducting has (3) and (4) as the objects. For example, the preparation of the monatomic layer ferromagnetic materials and the elucidation of their properties are the targets. This research has yielded information on the structure of the

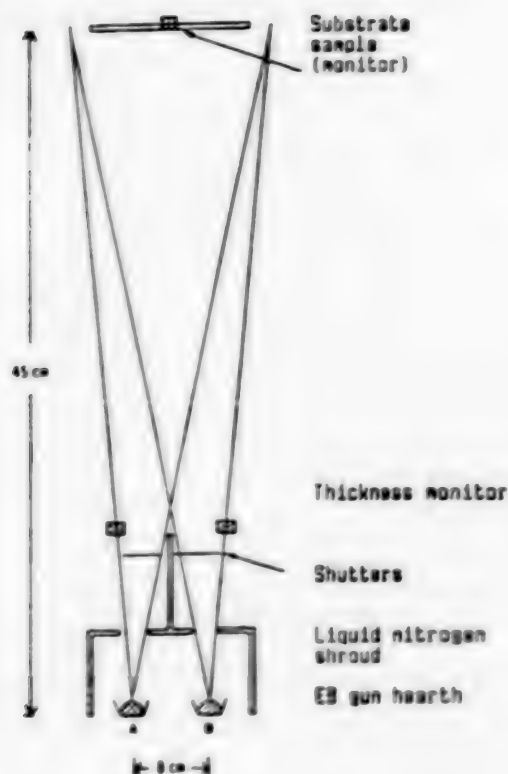


Figure 1. Sample Preparation System

multilayer film and information is available regarding to what degree the structure as designed has been microscopically realized. An artificial superlattice can be so designated only when the artificial period length of the multilayer film becomes short, about several atomic layers; it must be considered a new material and no longer a combination of two materials. The artificial superlattice exists only in the nonequilibrium state and is a new material that has controlled the microstructure. It has come to attract attention as new material having elements previously not included within the concept of materials up to now. Although it has not yet reached the stage of leading to great practical use, considerable results have already been achieved as the object of basic research. We will introduce several of the research projects which we have carried out and explain to what extent control on the structure is possible.

2. Fe-Mg Artificial Superlattice

Artificial superlattices, when considered from the structure, can be largely classified into two types: the epitaxial and the nonepitaxial type. Since Fe and Mg, respectively, have the bcc and hcp structures and the radius differs by more than 20 percent, the Fe-Mg artificial superlattice is a typical example of the nonepitaxial artificial superlattice. Needless to say, the artificial superlattice is a new material because it is a combination of neither melting together nor forming an alloy even in the liquid phase. X-ray diffraction and electron microscope observation of the sample section are used to study whether or not an artificial period has

been prepared in the multilayer film prepared by the alternate vacuum deposition method.

It has been found that a superior artificial period can be prepared. For example, the electron microscope photo of the microtome cut section of the sample with the Fe layer of 4 Å and the Mg layer of 16 Å is shown in Figure 2. It is clear that the structure of the sample was homogeneous and a smooth interface was continuously prepared despite the fact that the artificial period was 20 Å and the Fe layer was only two atomic layers. Therefore, an ultrathin Fe layer sandwiched by the Mg layer was available. The magnetism of such an Fe monatomic layer has been studied through Mossbauer spectroscopy and magnetic measurement, and the Mossbauer spectrum of the 1 Å Fe layer has indicated a very different intensity ratio than that of 15 Å (Figure 3). This indicates that the direction easy for magnetization has changed to a direction perpendicular to the film surface and this is one of the peculiarities of the magnetism of the Fe monatomic layer.

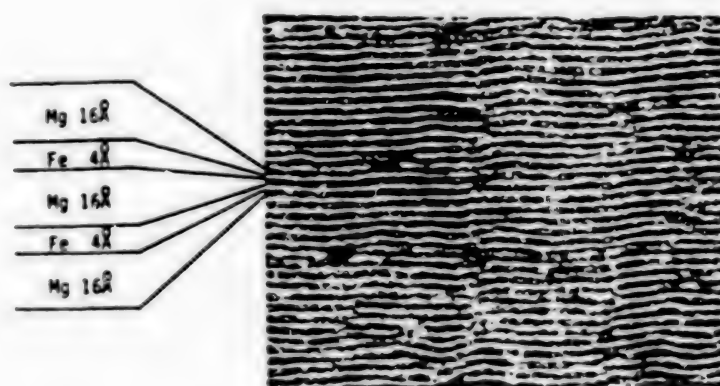


Figure 2. TEM Observation of $[\text{Fe}(4\text{\AA})/\text{Mg}(16\text{\AA})]_n$ Superlattice

3. Mn-Sb Artificial Superlattice

As mentioned, the Fe-Mg artificial superlattice is a nonepitaxial artificial lattice, it takes on an amorphous structure when the thickness of the Fe layer is less than 10 Å and it is difficult to clarify its structure microscopically. On the other hand, the example that has brought about the ferromagnetic monatomic layer in the epitaxial artificial superlattice is the Mn-Sb artificial superlattice. Both Mn and Sb do not have ferromagnetism but the compound MnSb indicates ferromagnetism. The reaction of Mn and Sb is great and compound layers are formed when they are stacked at room temperature. It has been found that a ferromagnetism monatomic Mn layer sandwiched by Sb is created when the nominal thickness of the Mn layer is 1 Å. Moreover, the atomic configuration in the periphery of the Mn atom can be estimated as it is epitaxially formed with the Sb layer. The interesting thing is that this system, similar to the Fe-Mg system, has its direction of easy magnetization on the monatomic layer in a direction perpendicular to the surface and the magnetization transfers to the in-plane direction when the thickness of the Mn layer becomes more than three atomic layers.

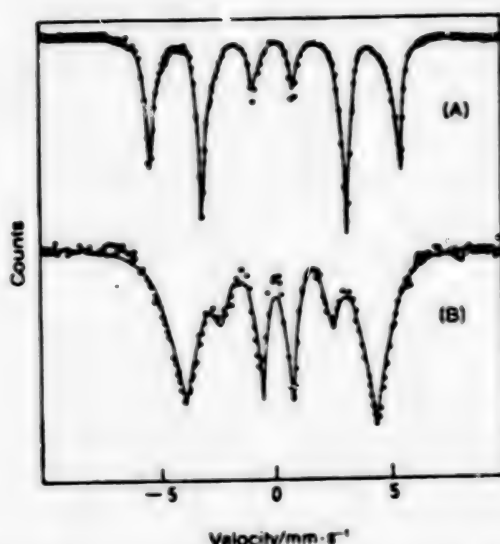


Figure 3. Mossbauer Absorption Spectra of Fe-Mg Superlattice. The thicknesses of individual Fe layer are (A) 15 Å and (B) 1 Å

4. V-Ag Artificial Superlattice

Several results have also been obtained in the basic research on superconductivity using the artificial superlattice as the sample. The Ag layer also becomes superconductive to a certain degree by the proximity effect in case of the artificial superlattice stacking the superconductive metal V and the ordinary conductive metal Ag. Whether the entire sample becomes a superconductor or the various V layers become a two-dimensional superconductive layer is determined by comparing the thickness and interference length of the Ag layer. Such dimensionality research in superconductivity was conducted on the V-Ag artificial superlattice. According to the phase diagram classification, V and Ag similar to the Fe-Mg system are of the two-liquid separation type and although the V-Ag artificial superlattice is a new material, the superconductivity transition point always becomes lowered when the artificial superlattice of V and Ag is realized. Therefore, research is presently being carried out on an artificial superlattice which combines V with substances other than Ag to obtain the factor that raises the transition point. V is of the bcc structure and it is also of the bcc-type structure in the V-Ag artificial superlattice when the thickness of the V layer is more than 10 Å. However, it has been discovered that it becomes an fcc-type by the epitaxy with Ag when the V layer is several Å and it has a weak magnetism at low temperatures. This is an example where a semiequilibrium crystal structure has been realized by an artificial superlattice.

5. Conclusion

We have introduced actual examples of the basic research on metallic superlattices and have explained to what extent the microscopic material

design was possible. Although studies have just begun on the artificial superlattice as a material for practical use, the artificial superlattice contains new elements not seen before and the extent of its mystery is linked to future expectations.

20158/9365

ICB Techniques Used for Film Formation

43063803f Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 112-114

[Text] **Abstract:** The ionized cluster beam (ICB) method is one of the novel ion assisted techniques for film formation. The clusters, aggregates of 100-2,000 atoms, are formed by condensing pure vapor of normally solid materials in an adiabatic expansion process. In ICB deposition, the beam of clusters is partially ionized and accelerated toward the substrate. Peculiar properties of the clusters as well as their kinetic energy and charge result in special film formation conditions. This technique allows unique film formations, such as low temperature epitaxy, hetero-pitaxy with large lattice misfit, formation of ultrathin films and very smooth film surfaces. It enables control of crystal structure, chemical composition, and various electrical properties of the film. Fundamental characteristics of ICB process and possibility of forming new materials are discussed. Some examples of the films deposited by ICB method and their properties are also given.

1. Introduction

Since the mechanism forming thin films can be controlled by the amount of kinetic energy and electric charge of grains reaching the substrate in a thin film formation technology using ions, the formation of various thin films having characteristics not available with the conventional thermal equilibrium method becomes possible. The vapor deposition method of the ionized cluster beam (ICB) is a unique technology developed by us and it is capable of ionizing the cluster of about 100 to 2,000 atoms mutually bonded loosely, providing acceleration by the electric field and transporting them on the substrate and yielding a high-grade thin film formation, including new materials creation and crystal growth.

2. Characteristics of ICB Method

(1) The ICB method makes it possible to achieve energy sufficient for film formation, i.e., a low acceleration of less than several hundreds of eV and especially from 100 eV to less than 200 eV. It is capable of avoiding the damage caused by electrical charge in the atmosphere and transporting a large capacity beam on the substrate. It can also be applied to organic as

well as inorganic materials such as metals, semiconductors, insulators, magnetic materials, ceramics, etc.

(2) The cluster decomposes into individual atoms when it jet collides the substrate and the surface dispersion energy is increased and freely controlled by the incident energy converted in the substrate surface direction (migration effect). In other words, the cluster can be controlled freely from amorphous to a single crystal in a three-dimensional state by changing the incident energy while the temperature of the substrate stays low.

(3) A portion of the kinetic energy which the cluster has been utilized to purify the substrate and the deposition surfaces at the start of or during vacuum deposition. In other words, since impurities and foulings that have physically and chemically bonded are removable and vacuum deposition can be continuously conducted without breaking the vacuum condition, preparation of thin films with high purity is possible.

(4) Critical parameters such as the cohesive core formation, cohesive core growth, and cohesion in the initial process of film formation are controllable and the crystallizing property of the vacuum deposition films are also freely controllable.

(5) The adhesion probability between the substrate and vacuum deposited material or vacuum deposited grain can be sharply controlled by the acceleration voltage and the mixing quantity of the ionized clusters, and the x of A_xB_{1-x} can be artificially controlled when synthesizing both the A and B materials.

(6) The film formation of semiconductors, insulators, etc., not to mention metals is easy without any damages caused by the space electric charge effect when sufficiently utilizing the electric charge effect possessed by the ion.

(7) Film formation (multiple nozzle method, multiple crucible method) is possible at a suitable vacuum deposition speed and in a large area by using the ordinary high-vacuum domain (10^{-11} to 10^{-6} torr) and the film has performance suiting industrial applications. On the other hand, the ultrahigh vacuum domain (10^{-11} to 10^{-10} torr) is useful for investigating the thin film formation process and the in-situ observation of the crystallizing property, etc., is possible by using this vacuum domain.

(8) The preparation of oxidized films, nitrified films, hydrogenated films, and fluoridized films is possible with a superior controllability by utilizing the fact that the radicals generated in the ion and ionizing processes are chemically active in the ICB technology in reactive gas atmosphere (reactive ICB, i.e., R-CIB technology).

3. ICB Vacuum Deposition Device

The basic configuration of the ICB vacuum deposition device is shown in Figure 1. The electron flow is irradiated on the cluster generated by

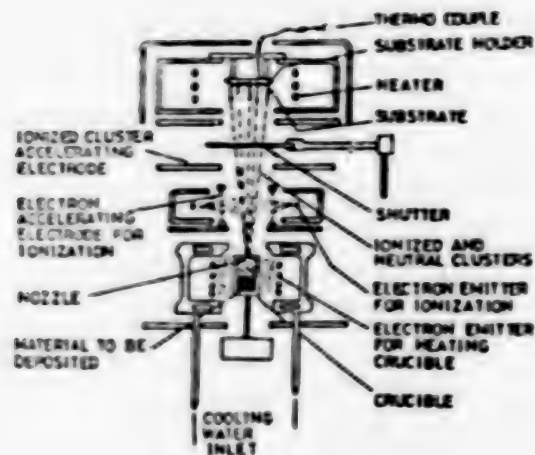


Figure 1. Configuration of ICB Vacuum Deposition Device

jetting the vacuum deposited material vaporized from the crucible nozzle, a portion is ionized to univalent and made the cluster ion and this is jet collided to the substrate by accelerating it by the negative voltage V_a applied to the acceleration electrode. The acceleration voltage V_a and the electron current I_e for ionization can be suitably selected according to the substrate material, vacuum deposited material, and the intended film quality. The ICB method as seen here is suited for film formation in high vacuum and it has the advantage that the incident energy to the substrate and the ion mixing quantity can be freely controlled.

In the R-ICB method, the metal steam cluster is vacuum deposited in a thin reactive gas atmosphere like oxygen and nitrogen and a thin film of oxides and nitrides is obtained. Besides this method, the method of jointly using vacuum deposition and injection that has used a small-sized microwave ion source in combination with ICB vacuum deposition has also been developed. The structure of this device is shown in Figure 2.

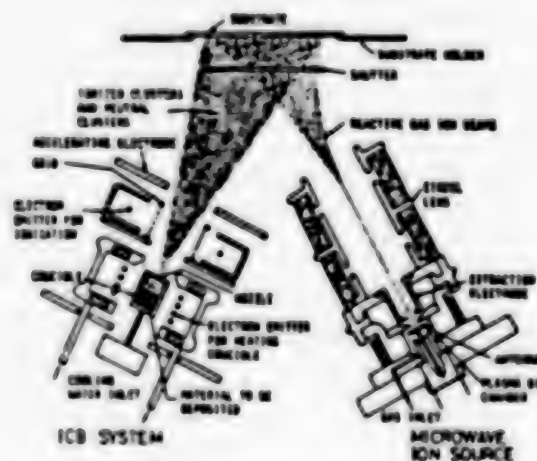


Figure 2. Conceptual Drawing of Combined ICB-Microwave Ion Source-Type Device

4. Example on the Development of Inorganic Materials Such as Metals, Semiconductors, Insulators, Etc., by the ICB Method

(1) The epitaxial growth of materials with a large lattice unconformity (for example, metals on a semiconductor) is possible. When the ICB method is used, the epitaxial growth of Al is possible on an Si substrate in room temperature irrespective of the presence of lattice unconformity amounting to 25 percent. The epitaxial Al film excels in thermal stability and there is hope in this film as electrodes and wiring materials of integrated circuits.

(2) In addition to controlling the crystallizing property and interface characteristic, the characteristics of the thin film formation using ion are that the stress in the film can be eased and atomically flat film without cracks can be formed even with materials with a large difference in the coefficient of thermal expansion. For example, the CaF_2 film that has been vacuum deposited on Si (111) by various acceleration voltages performs epitaxial growth and a surface without cracks and with small unevenness composed by an ultrafine crystal surface has been available. In addition to this, the Al (111) film was grown and the monocrystal MIS structure was prepared.

(3) The ICB method can also be effectively used in the crystal growth and crystal control of complicated compound semiconductors and in the realization of extremely thin and multilayered films. For example, the CdTe-PbTe extremely thin and multilayered structure of CdTe and PbTe was prepared by using the dual crucible system. As the result of growing a CdTe buffer layer of 1,500 Å on InSb under the acceleration voltage of 5 kV, substrate temperature of 200°C and vacuum depositing 60 layers of the CdTe and PbTe ultrathin layers alternately on top of this buffer layer, a superlattice effect was optically indicated. The measured photon energy coincided well with the theoretical energy value and it is presently conducted on all layers to the thinness of 15 Å.

(4) Extremely good quality of oxidized films and nitrified films are available with good controllability under the substrate temperature of about 100°C in the joint use method of the ICB ion source and the microwave ion source. This has been demonstrated with SiN, AlN, Al_2O_3 , etc.

5. Development Examples of Organic Materials by ICB

The application of organic thin films prepared by vacuum deposition to electronic devices is possible. Thin films formed as examples of an organic semiconductor by using copper phthalocyanine and those formed as examples of the organic insulator using polyethylene had few impurities and a high crystallizing property. Moreover, control of various electrical characteristics and interface characteristic, and doping, etc., of organic semiconductors was also possible. Thin film type transistors using copper phthalocyanine and the MISFET, using polyethylene were prepared and it has been shown that the ICB method is also a promising method in the development of organic thin film type electronic devices. Since this method is a process carried out in high vacuum, it excels in

controllability as the vacuum deposition conditions can be freely controlled electrically and yet automatically from the exterior. This method is believed to be effective for the development of new organic materials in the future.

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20158/9365

Toughening Ceramics by Micro, Nanostructure Design

43063803g Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 115-117

[Article by Koichi Niihara, Physics Department, National Defense Academy]

[Text] **Abstract:** The mechanical properties of ceramics are strongly dependent on their micro and nanostructures. The toughening and strengthening of Al_2O_3 , Si_3N_4 , and SiC ceramics by controlling the micro and nanostructure are reviewed in this article. The micro and nanostructure are designed by incorporating second phases or structural defects into grain boundaries and/or inside grains. For the Al_2O_3 ceramics, the three-fold increase in fracture toughness and strength is achieved by dispersing the superfine SiC particulate and both ZrO_2 (2 mol% Y_2O_3) and SiC whisker. The Si_3N_4 ceramics consolidated from Si-C-N powder precursors indicate the excellent mechanical properties even at high temperatures. In this Si_3N_4 ceramics, the SiC particles are observed to be dispersed into grain boundaries and also inside grains. For the SiC ceramics, the crack-tip pinning and crack deflection by the stacking faults introduced into SiC grains are used to improve the fracture toughness.

1. Toughness and Strengthening Ceramics

The method to improve the fracture toughness of ceramics can be largely classified into two high-degree toughening methods: the method that introduces heterogeneous materials (crystal grains with different second phase, shape and dimension, intergranular phase, structural defect, etc.) into the sintered materials of simple structure and utilizes the interaction between the heterogeneous material and the cracks, and the method that shields the external stress by the process zone in the tip area of cracks generated by the heterogeneous materials. Mechanisms such as the pinning and bending of the crack tip, deflection of crack, and slanting of crack, are known in the former method. Mechanisms such as the stress induced transformation of ZrO_2 , generation of micro cracks by the difference of thermal expansion and anisotropy, and the extraction of whiskers and fibers are known in the latter method. When considering the abovementioned high-degree toughening mechanism from the standpoint of structural control, it can be understood that the fracture toughness of ceramics is generally achieved by making the surface heterogeneous.

Therefore, it is generally difficult to tie the improvement of the fracture toughness of ceramics to the improvement of fracture strength. This is because the heterogeneous materials that have been dispersed work as the fracture source or work to facilitate the enlargement of the fracture source. Therefore, to link the high-degree toughness of such mechanisms to high strength and develop a tough ceramic, it is necessary to strictly adjust the dimension, shape, and distribution of the introduced heterogeneous materials and either control as much as possible the enlargement of the fracture source or simultaneously introduce the mechanism that controls the enlargement of the fracture source by the heterogeneous material. Recent research we have done on toughening ceramics by micro and nanostructure control will be introduced here.

2. Microstructure Control and Toughening

In case of the SiC and Si₃N₄ ceramics that are attracting the most attention as high temperature structural materials, a material having the fracture toughness of more than 6 MN/m^{3/2} has been developed by growing cylindrical grains and making the structure heterogeneous in the range of not enlarging the critical crack dimension and by the high-degree toughening that causes the deflection of the crack. We recently produced an Si₃N₄/SiC complex with the hybrid amorphous S-C-N powder as the starting source and succeeded in simultaneously improving the toughness and strength of the Si₃N₄ ceramic as shown in Figure 1. The dispersed SiC accelerates the growth of the Si₃N₄ cylindrical grains and improves the toughness (and therefore the strength) at approximately less than 10 wt%. Moreover, it plays the roles of decreasing the crystal grain size of the Si₃N₄ matrix, making the fracture source small and improving the strength at about more than 15 wt%. In addition it became clear, as shown in Figure 2, that the high temperature strength of the Si₃N₄ was also remarkably improved by the dispersed SiC. It was also found, according to the electron microscope, that many SiC grains were also dispersed in the crystal grains and not only in the grain boundary. Although it cannot be clearly defined now, there is a possibility that the SiC grains dispersed in these grains play an important role in the toughening of this system.

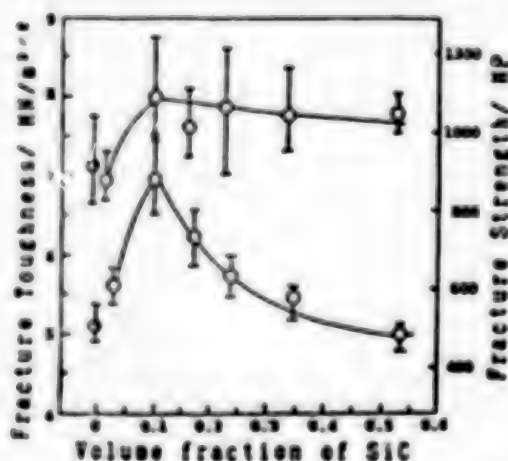


Figure 1. Toughness and Strength of Si₃N₄/SiC Complex

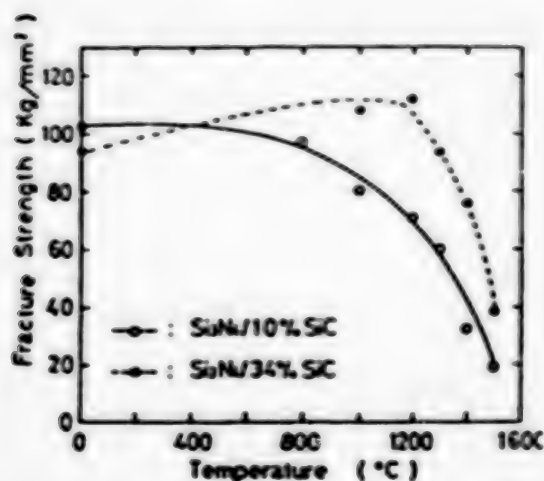


Figure 2. High-Temperature Strength of Si₃N₄/SiC Complex

3. Nanostructure Control and Toughening

The high-degree toughening of ceramics considered up to now was only the high-degree toughening by the micron order structure control that excluded the intergranular. However, there is a possibility that the toughness and strength of ceramics will be further improved when the smaller level in the crystal grain, i.e., the nanometer level structure control is considered. For example, various methods such as stacking the second phase for every nanometer in the crystal grain, compounding the second phase of the nano order in the crystal grain and introducing the twin or stacking fault in the crystal grain, can be considered. This is an attempt to reduce the brittleness of ceramics more substantively by controlling the crystal structure of the grain, which is considered the minimum unit of ceramics.

We have recently introduced a stacking fault in the crystal grain and have attempted to improve the SiC fracture toughness by causing a crack deflection at an extremely micro level. As a result, it was found that the fracture toughness of SiC with few stacking faults was 3.1 MN/m^{3/2} but the fracture toughness of SiC with many stacking faults indicated an extremely high fracture toughness of 6.8 MN/m^{3/2}. The strength characteristic of the Al₂O₃/SiC nano composite material that has achieved toughening by dispersing the SiC grains in the crystal grain boundary and crystal grains and realizing the high-degree toughening and conscious reduction of the fracture sources is shown in Figure 3. The strength of 1,500 MPa which is more than three times that of the ordinary Al₂O₃ ceramics has been achieved. This is because generation of the fracture source has been controlled to a considerable degree by the compressive residual stress generated in the periphery of the dispersed SiC grains in the crystal grains and the fracture source has decreased to one-tenth of what it was. Figure 4 shows the temperature change of the Al₂O₃/SiC nano composite material. The results seen in Figure 4 indicate that the nano compounding of ceramics not only exhibits its power in the improvement of toughness and strength at room temperature but also in the improvement of high temperature characteristics.

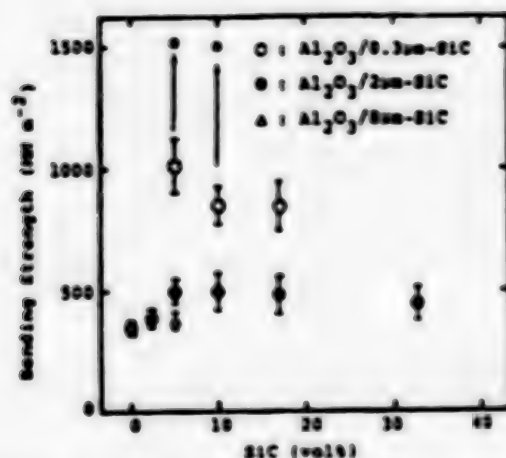


Figure 3. Strength Characteristics of Al₂O₃/SiC Nano Complex

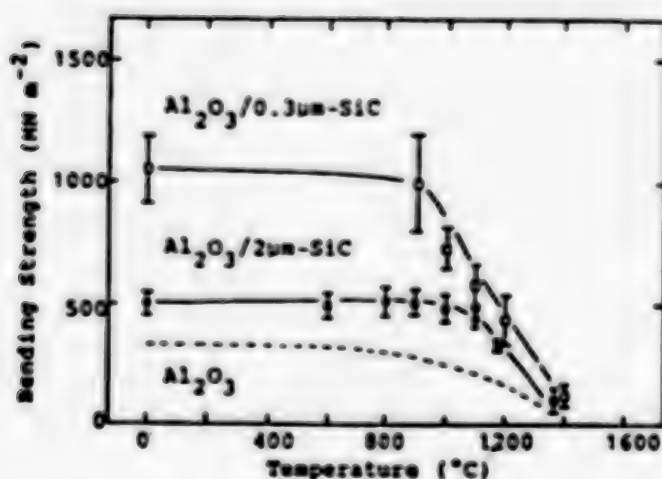


Figure 4. High-Temperature Strength of Al₂O₃ Nano Complex

4. Combination of Micro and Nanostructure Control (Multiple Toughening)

It is necessary to either realize a multiple toughening which independently allows a number of high-degree toughening mechanisms to work without damaging others or realize a combination of the micro and nanostructure control for breaking through the limit of an independent toughening mechanism. We have recently succeeded in improving the toughness and strength of Al₂O₃ by more than three times by dispersing ZrO₂ and SiC whiskers in Al₂O₃, and by making the most of practically all of the roles of the various dispersal phases. Moreover, we have succeeded in improving the toughness and strength of Al₂O₃ drastically through multiple toughening (combination of microstructure control and nanostructure control) by further compounding the SiC whiskers with the nano complex dispersing SiC grains in the crystal grains of Al₂O₃.

5. Conclusion

Research on the high-degree toughening of ceramics has progressed with rapid strides in the recent 10 years. The research focus has switched from improving toughness by microstructure control to utilizing the phase transformation of ZrO_2 . In recent years, many people have shown interest in high-degree toughening by utilizing whiskers and fibers. Moreover, research on multiple toughening is also being promoted. With regard to microstructure in relation to toughness, an idea has come up to improve toughness by a microstructure control at a nano order which is 1/1000 of that which exists. We firmly believe that this research will bear fruit without fail and lead to the development of tough ceramics having both characteristics of both ceramics and metals. Ceramics will become the material that is truly indispensable in this world and one that will challenge the future advanced technologies when this development is realized.

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Progress in Membrane Separations

43063803h Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 127-129

[Article by Tsunesuke Doi, Research Association for Basic Polymer Technology]

[Text] **Abstract:** Since ion exchange membranes were produced in the early 1960's in Japan, the technology of membrane separations has remarkably progressed, and nearly all kinds of industrial membranes have become available in Japan. However, the original concepts and prototypes were imported from Western countries with few unique Japanese innovations. Thus both the government and the private sector have emphasized research and development for new membrane separation technology.

In this paper, recent progress in membrane separation including our experimental results will be reported.

1. Progress of Liquid Separation Membranes

Explanations made here will be mainly limited to industrial separation membranes. The industrial separation membranes can be largely classified into the liquid separation membrane and the gas separation membrane.

With the dialytic membrane as the first instance, the liquid separation membrane already has a history of more than 60 years. The application range of the dialytic membrane has also expanded in the medical field in addition to industrial utilization. It presently occupies an important position as a hemodialysis membrane and steady research on improvement is promoted.

At the beginning of the 1960's, the ion-exchange membrane appeared on the stage and it came to be used for turning seawater and salt water into fresh water, production of salt by the concentration of seawater, and the production of caustic soda and chlorine by salt electrolysis. Particularly, substitution of the salt electrolysis by the mercury and diaphragm processes by the ion exchange membrane process may be called a technological innovation. It can be said that this is proof of the ion exchange membrane becoming advantageous in comparison to the conventional

pprocesses not only from the quality aspect but also from the cost aspect that has been brought about by the incessant improvements added. Following the ion exchange membranes, the reverse osmosis membranes, ultrafiltration membranes, and precision filter membranes enter the stage. The reverse osmosis membrane plays a big role in turning seawater into pure water and a membrane with a low pressure and high transmittance flow rate is being developed. All of the reverse osmosis membranes, ultrafiltration membranes, and precision filter membranes are highlighted and are used for the production of pure water and ultrapure water, separation, removal, and concentration of fungus and corpuscular substances.

Research on the ultrafiltration membranes is centered around research on the improvement of thermal resistance, chemical resistance, and solvent resistance. Moreover, research on pollution prevention, etc., has become important regarding the precision filter membranes.

The driving force of the process applied in the abovementioned separation membranes that have been put to practical use is either the pressure difference by pressurization, temperature difference or potential difference. There is the osmosis vaporization process that has started to be put to practical use recently and its driving force is the pressure difference by pressure reduction. A considerably different focus will be necessary in the development method of the separation membranes and especially of the hollow fiber type separation membrane which is applied depending on if the pressure difference is caused by pressurization or by pressure reduction.

It may be necessary to constantly pay attention to the membrane reactor as the future broad-based industrial liquid separator.

The separation objects of the liquid separation membranes that have been put to practical use are all aqueous solutions. As long as it is called a liquid separation membrane, the ideal is that the separation of a wide range of liquids other than the aqueous solutions, i.e. the separation of nonaqueous solutions, is also carried out. However, research aimed at nonaqueous solutions is limited. The reason for this is that improvement of durability (solvent resistance) is difficult. Despite this fact, we believe that more attention should be turned toward research on nonaqueous solution separation.

2. Progress of Gas Separation Membranes

We will mention the gas separation membranes next.

It has been known since the olden days that permeability differs according to the type of polymer membrane and gas when gas permeated the polymer membrane. However, historically speaking the period when research intending to utilize a gas separation membrane as the industrial separation membrane was begun and the period when it actually came to be industrially utilized took longer than did the liquid separation membrane.

Although research on the oxygen-nitrogen separation membrane has been actively carried out up to now, helium separation from natural gas, olefin-paraffin separation membrane and the separation membrane of sulfur dioxide and hydrogen sulfide in the stock gas, it is difficult to say that it has reached the stage of being put to practical use. However, it is worthy of special note that the Monsanto Chemical Co. finally succeeded in industrializing a composite hollow fiber membrane on the hydrogen separation from the various mixed gases after learning lessons from the failures of other companies at the initial period in the research and development of thermoplastic polymers by simple hollow fiber membranes.

3. Status Quo of Research and Development Results

Lastly, I will mention the recent research conditions around our research results.

We are conducting research in accordance with the Project of Basic Technology for Future Industries started under a 10-year project by the Agency of Industrial Science and Technology, MITI, in 1981. We are aiming at the development of a high effective liquid separation membrane, gas separation membrane, and their related technologies making possible the separation, concentration, and purification of substances that lead to excessive energy consumption in the conventional separation processes (for example, water-alcohol) and substances in which the separation and purification were difficult due to their physical and chemical characteristics being extremely close (such as the isomer). It may be said that the main point of the research and development lies in the creation of a controlled new separation membrane having the structure of a higher order and possessing a suitable functional group or carrier. The types of membranes can be classified into the solid membrane and the liquid membrane. It is a fact that having the advantage of making the basic knowledge gained by our predecessors on the industrial separation membranes our foundation for research and development of separation membranes, this knowledge will also create a high hurdle for rapid progress. Therefore, greater efforts are necessary. The main contents are as follows in reporting our results obtained on the Project of Basic Technology for Future Industries when compared with the status quo of the world.

(1) Liquid separation membranes

| | |
|---|--|
| --Water ethanol separation membranes | Water priority transmission membrane Ethanol priority transmission membrane |
| --Water-acetic acid separation membrane | Water priority transmission membrane |
| --Amino acid separation membranes | Isomer separation membrane Concentrated membrane |

--Nonaqueous solution separation
membrane

(2) Gas separation membranes

--Oxygen-nitrogen separation membrane

--Carbon monoxide-nitrogen separation
membrane

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Polymer Chain Conformation, Membrane Permeability

430638031 Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 132-135

[Article by Akio Nakajima, Department of Applied Chemistry, Osaka Institute of Technology (No 5-16-1, Ohmiya, Asahi-ku, Osaka 535, Japan)]

[Text] **Abstract:** Needless to say, a distinctive feature of polymer chain molecules is the capability to form fiber and membrane owing to their long chain structure. Thus, the polymer membranes have been used in versatile fields. Among which, membrane separation technology is the latest surge of interest, and covers various applications as gas separation, ultrapure water production for electronics uses, desalination, waste water treatment in metal finishing industry, ion exchange, electrolysis diaphragm, liquid separation, and a variety of uses in biotechnology, e.g., plasma pheresis, artificial kidney, artificial skin, artificial lung, and membrane bioreactors. Many separation problems are being solved, however, some have not yet reached commercial viability.

Here I mention fundamental concepts and recent trends on gas separation and liquid separation by polymer membranes in connection with the molecular structures and conformations of the component polymers, and membrane separation as biomaterials and bioreactors.

1. Membrane separation of gas mixture
2. Membrane separation of liquid mixture
3. membrane separation as biomaterials and bioreactor

The most outstanding characteristic of the polymer chain molecules is the capability of forming fibers and membranes that are attributable to the long chain structure. Therefore, polymer membranes have been utilized in various fields since the olden days. However, the main concern recently is the membrane separation technology. There are various applications of biotechnology related fields such as plasma separation, artificial kidney, artificial skin, artificial lung, membrane bioreactor, contained in this technology besides the gas separation, production of ultrapure water for the electronics industry, turning salt water into pure water, effluent treatment in the metal processing industry, ion-exchange, electrolytic membrane, and liquid separation. Those with a membrane separation

technology have already established their industrial basis and there are also quite a few fields in which future development can be expected.

From the standpoint of the molecular structure and chain conformation of polymers constituting the membranes, descriptions will be made on the basic concept and recent results obtained on the gas separation and liquid separation by polymer membranes and in addition, remarks will be made in this text on the membrane separation as a biomaterial.

1. Membrane separation of gas mixture

The following equation (1) is given for the gas flow rate (Q) that crosses the polymer membrane with the thickness of d and the area of A by the pressure difference of Δp .

$$Q = DS \frac{A \Delta p}{d} = P \frac{A \Delta p}{d} \quad (1)$$

The permeation coefficient (P) is indicated by the product of the diffusion coefficient (D) of gas in the membrane and the absorption coefficient (S) of gas to the membrane. The selectivity α of the membrane separation of the two component gas mixtures (A and B) is defined by the following equation with the partial pressure difference of the i component before and after the membrane transmission as Δp_i .

$$\alpha = Q_A/Q_B = \frac{P_A \Delta p_A}{P_B \Delta p_B} \quad (2)$$

The collision diameter of gas is an important factor in discussing D and S. The collision diameter of simple gases are shown in the following table.

| Gas | He | H ₂ | O ₂ | CO | N ₂ | CH ₄ | Co ₂ |
|------------------------|------|----------------|----------------|------|----------------|-----------------|-----------------|
| Collision diameter (Å) | 2.58 | 2.81 | 3.44 | 3.62 | 3.68 | 3.82 | 4.00 |

The gas permeability of the nonporous polymer membranes has a close relationship with the structure, conformation and behavior of polymer membranes in the amorphous state. The author Nakajima and his group³ have discovered by the X-ray small-angle scattering method that the polymer chain conformation in the morphous state was achieved by the nonperturbed chain dimension, e.g., by the square mean $\langle R_0^2 \rangle$ of the distance between the nonperturbed chain ends. The nonperturbed dimension $\langle R_0^2 \rangle$ of the virtual free rotation chain composed by the linkage of the carbon atoms is given by the equation of $\langle R_0^2 \rangle_f = \frac{1 - \cos \theta}{1 + \cos \theta} N b^2$ (whereas, θ = bond angle, b = bond

length, N = number of bonds). Therefore, when the objective polymer nonperturbed dimension is made $\langle R_0^2 \rangle$, $\langle R_0^2 \rangle / \langle R_0^2 \rangle_f$ is deemed as the scale of chain flexibility or the chain behavior. The following table indicates the values⁴ of the energy barrier height impeding the free rotation around the bond obtained in low molecular compounds. The rotation energy barrier of

the C-O bond, C-S bond, C-C bond neighboring the C-C bond and C-Si bond have a considerably low value. These results are important when discussing the conformation of long chain molecules.

| Bond | $H_3C_2CH_3$ | $H_3C_2CH=CH$ | $H_3C_2S-CH_3$ | $H_3C_2SiH_3$ | $H_3C_2O-CH_3$ | $H_3C_2CCl_3$ | $H_3C_2CF_3$ |
|--------------------------|--------------|---------------|----------------|---------------|----------------|---------------|--------------|
| Height of barrier (Kcal) | 2.8 | 1.9 | 2.0 | 1.5 | 1.6 | 2.9 | 3.0 |

It is known that rubber-like polymers such as the silicon rubber and natural rubber indicate a far higher permeability than polymers with a small flexibility such as the cellulose derivatives. Moreover, polymers with a rigid skeletal chain indicate a conspicuous decrease of D together with the increase of the collision diameter of the gas molecules and therefore, the selectivity (separation coefficient) of this type of polymer is greater than that of the rubber-like polymer. The molecular design of membrane polymers is made according to such a basic concept. Several of the practical uses are: the polydimethyl siloxane used in the H_2 separation from purge gas and O_2 separation from air, poly-4-methylpentane 1 used in the N_2 separation from air, and the cellulose acetate used in the CO_2-CH_4 separation.

P and α are of a specific gas-polymer system and have specific values in an ordinary membrane separation. The method for achieving a higher permeability and selectivity is the utilization of active transport using a suitable carrier. In the research on the Project of Basic Technology for Future Industries (JITA), the membrane systems of $Q_{CO} = 3 \times 10^{-8}$ and $\alpha(CO/N_2) = 190$ have been developed in the Cu salt/N-methylimidazole carrier and the membrane systems of $Q_{O_2} = 10^{-8}$ and $\alpha(O_2/N_2) = 34$ have been developed in the $Co(SCN)_2/H_2N(CH_2-CH_2-CH_2NH)_3$ carrier. However, the unit of transmission speed (Q) is $cm^3/cm^2 \cdot sec \cdot cmHg$.

2. Membrane separation of liquid mixture

Equation (1) with S as the solubility coefficient is applied in the liquid transmission by the nonporous polymer membranes and the selectivity $\alpha(A/B)$ of the membrane is expressed by equation (3) with c_A^0 and c_B^0 as the initial concentration of A and B, and c_A and c_B as the concentration after the membrane transmission.

$$\alpha(A/B) = \frac{c_A^0 c_B^0}{c_B c_A} \quad (3)$$

The solution process is far superior to the diffusion process in the liquid separation by the osmotic vaporization method and the solution parameter δ_1 and the dipole moment μ_1 of the liquid are related to permeability. In the research carried to at the Industrial Products Research Institute of the Agency of Industrial Science and Technology, it was made clear that the liquid flux by the polyethylene membrane became larger as the δ_1 came closer to δ_p of the polymer, it declined as $|\delta_1 - \delta_p|$ decreased and the water selectivity $\alpha(W/E)$ by various polymer membranes from the water-ethanol

system was the function of $\delta_w - \delta_p$. On the other hand, Garden⁶ recognized the interrelation between the δ_p and the critical surface tension γ_c of polymers and the difference between the surface tension γ_l of the liquid and the γ_c of polymer may be serviceable in the evaluation of the polymer compatibility. The relationship of cluster⁷ with water must be taken into consideration when it comes to the water system mixed liquids. The cluster size becomes small and the number of clusters increases when a different component is added in the water. This is why the flux and selectivity of water from the water-ethanol mixture are controlled by the ethanol content.

In the JITA project, polymers with a rigid skeletal chain were studied for the separation of liquid mixtures such as water-ethanol and water-acetic acid, by the osmotic vaporization method. The cellulose derivative, chitosan and alginic acid were used in the water selective separation from the water-ethanol, the substituted polyphenyleneoxide and substituted polyacetylene were used in the ethanol selective separation from the ethanol-water and the polyimido and polyalamide adjusted by the hydrophilic group were used in the water selective separation from water-acetic acid. It has been shown through the solid high resolution¹³ C-NMR research that the resolution increase by the ionization of the chitosan and alginic acid membranes closely relates to the change of the chain conformation based on the dihedral angle of the β -1,4 glucoside bond. Regarding the polyacetylene and polyphenyleneoxide derivatives, the selective transmission of ethanol is accelerated by the introduction of a bulky side chain with great mobility. Moreover, it is said that the water selective transmission of polyalamide having a strong electrolytic group like the sulfonic acid and crosslinked with polyhydric metal ions is caused by the strong interaction between the water molecules and the electrolytic group. The obtained α and Q values on chitosan were $\alpha(W/E) = 7000$ (E, 90 percent) and $Q = 1 \text{ kg/m}^2\text{h}$; those on the alginic acid were $\alpha(W/E) > 10,000$ and $Q = 1 \text{ kg/m}^2\text{h}$; those on the substituted polyacetylene were $\alpha(E/W) = 15$ and $Q = 0.3$; and those on the substituted polyamide were $\alpha(W/A) = 650$ and $Q = 0.17$.

3. Membrane separation of biomaterials and bioreactor

Well-known application examples are the artificial kidney and the artificial lung. The artificial kidney is the hemodialysis and ultrafiltration (uF) removal of metabolites such as urea, creatine, uric acid, and medium molecular weight substances. The ethylene-vinyl alcohol copolymer and polyacrylonitrile, are used for this purpose. The selective transmission mechanism of the porous membrane in the ultrafiltration method has been discussed by Kamide, et al.⁸ The artificial lung involves the introduction of oxygen and the release of carbon dioxide in the blood by membranes. Oxygen enrichment membranes such as silicon and porous membranes such as PP and PTE are used. Consideration of blood affinity with materials is indispensable in applying the polymer membranes to biomedical fields. Please refer to references 9 and 10 on progress in this area.

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Optical Resolution of Amino Acids by Supported Liquid Membranes

43063803] Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 136-138

[Article by Toshi Shinbo, Koichiro Nishimura, and Tomohiko Yamaguchi, National Chemical Laboratory for Industry]

[Text] Abstract: Novel membranes for enantiomeric resolution of racemic amino acids are reported. The membranes were prepared by immersing microporous poly(propylene) film into o-nitrophenyl phenylether containing chiral crown ether as carrier. Two modes of amino acid transport were examined: One was the co-transport with perchlorate anion, and the other, the countertransport with cations (metal cations and proton). Many lipophilic amino acids were transported with good enantioselectivity, and the highest enantioselectivity was obtained for phenylglycine (Table 2). The fluxes and enantioselectivities of amino acids obtained under varying conditions are presented (Table 1 and Figure 1) and the mechanism of the enantioselective transport is discussed. [End abstract]

Membrane separation is a separation technology that has attracted attention in recent years. It has the advantages that continuous operations are possible and it is an energy conservation technology. However, the separation of compounds in which the structure and properties of the optical isomer, etc., are similar was difficult with conventional polymer separation membranes. Therefore, studies were made on separating and transporting the optical isomer of amino acid by using a separation membrane based on a new separation principle and called the impregnation type liquid membrane in this research. Results of this research up to now will be reported here.

The impregnation type liquid membrane was prepared by impregnating o-nitrophenyl phenyl ether in which a chiral (optical active) crown ether was dissolved in a porous polypropylene membrane (Duragard 2400). The membrane transmission speed (flux) of the amino acid was obtained by measuring with HPLC the quantity of optical isomers of the amino acid transported by this membrane from phase 1 to phase 2 of the two aqueous solutions facing each other (Phase 1: Acid solution of amino acid of racemic modification; Phase 2: Acid of neutral aqueous solution not containing amino acid).

Since the co-transport system that transports in the same direction as the anion by using the concentration difference of the anion as the driving force and the countertransport system that transports in the reverse direction to the anion by using the concentration difference of the anion as the driving force can be considered for the transport systems in transporting the amino acid (anion) with the crown ether as the carrier, studies were made on both systems.

1. Optical Resolution of Amino Acid in the Co-Transport System

Since there was no example where the amino acid was optical resolution transported in the impregnation type liquid membrane with the chiral crown ether as the carrier before beginning this research, first of all an evaluation of the performance of the chiral crown ether with the synthesizing method already known as a carrier was made. The flux of the D-body and L-body of the amino acid making the chiral crown ether as the carrier can be expressed as follows in the co-transport system.

$$J_i = PC^*K_{ext}^i S / (1 + K_{ext}^{\Sigma} S) \quad (i = D \text{ or } L)$$

Whereas, P = Transmission coefficient of the ternary complex of amino acid, crown ether, and ClO_4^-

C^* = Initial concentration of crown ether

K_{ext}^i = Sampling constant of i-body

K_{ext}^{Σ} = Sum of K_{ext}^D and K_{ext}^L

S = Product of the i-body concentration of amino acid and the concentration of ClO_4^-






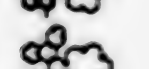

The performance of the crown ether as the carrier for the optical resolution of amino acid can be qualitatively evaluated by the parameters

of P, K_{ext}^{Σ} , K_{ext}^D/K_{ext}^L ($= J_D/J_L = \alpha$, optical resolution ratio). Various parameter values of the chiral crown ether are shown in Table 1. As clear from Table 1, the No 3 crown ether indicated the largest values in the optical resolution ratio, extremely great values were also indicated on P

and K_{ext}^{Σ} and it was known that it was the most superior carrier. Table 2 shows the results when transporting the various amino acid racemic modifications with the No 3 crown ether (R-body) as the carrier. Many amino acids have been enantioselectively transported with a superior separation ratio. In particular, the maximum optical resolution ratio was obtained in the phenylglycine.

Next, considering that the No 3 crown ether in Table 1 was the most superior carrier among the already known crown ethers, several types of chiral crown ethers having the 3,3'-diphenyl-1,1'-pinabutyl group as the basic optical active group and possessing another optical active group have been synthesized and their amino acid enantioselective transport activity were measured. Those indicating an optical resolution superior to the No 3 crown ether in Table 1 against specific amino acids were also available.

Table 1. Parameters of Chiral Crown Ethers

| Crown Ether | Form | P $10^{-4} \text{ cm s}^{-1}$ | K_{ext}^c 10^2 M^{-1} | Optical Resolution Ratio | Dominant Enantiomer Transported |
|---|------|------------------------------------|---|--------------------------------|---------------------------------------|
| 1  | S | - | - | - | - |
| 2  | R | 7.8 | 1.9 | 1.5 | L |
| 3  | R | 8.7 | 5.1 | 15.5 | D |
| 4  | R* | 6.0 | 2.2 | 1.2 | D |
| 5  | P | 1.8 | 2.0 | 1.2 | D |
| 6  | S | 6.2 | 12.2 | 1.9 | D |
| 7  | - | 7.8 | 4.7 | 1.0 | - |

Phase I: Racemic phenylglycine-ClO₄ in 0.5 M H₂SO₄.

Phase II: 0.05 M H₂SO₄.

Membrane: 0.05 M crown ether in o-nitrophenyl phenylether.

*) 32 % e.e. **) achiral crown ether.

Table 2. Enantioselective Transport of Amino Acid Perchlorates Through the Supported Liquid Membrane

| Amino acid | Form | Run time/h | Flux / $10^{-7} \text{ mol cm}^{-2} \text{ h}^{-1}$ | | $\alpha = J_D/J_L$ |
|---------------|-------------------|------------|---|-------|--------------------|
| | | | J_D | J_L | |
| Phenylglycine | rac ^{al} | 12.7 | 5.97 | 0.26 | 22.7 |
| Tryptophan | rac ^{al} | 12.7 | 4.66 | 0.69 | 6.7 |
| Phenylalanine | rac | 12.7 | 3.99 | 0.55 | 7.2 |
| Leucine | rac | 25.5 | 3.87 | 0.29 | 13.5 |
| Isoleucine | rac | 12.0 | 1.11 | 0.07 | 15.0 |
| tert-Leucine | rac | 25.5 | 0.42 | 0.03 | 13.4 |
| Methionine | rac | 25.3 | 3.40 | 0.32 | 11.2 |
| Valine | rac | 25.5 | 0.75 | 0.10 | 7.7 |
| Tyrosine | rac ^{al} | 47.0 | 0.26 | 0.04 | 6.0 |

Phase I: 0.1 M racemic amino acid in 0.05 M HClO₄ + 0.05 M H₂SO₄.

Phase II: 0.05 M (^{al}0.5 M) H₂SO₄.

Membrane: 0.05 M chiral crown ether (R)-3 in o-nitrophenyl phenylether.

however, a carrier exceeding the No 3 ether crown has not been obtained up to now. Explanations will be also made on the results.

2. Optical Resolution of Amino Acid in the Countertransport System

As impregnation type liquid membrane containing a fat soluble anion as the co-carrier together with the chiral crown ether as the carrier was used in the countertransport system. Upon investigating the effect as a carrier on various fat soluble anions, it was found that the dinonyl naphthalene sulfonic acid had a great flux, there was elution from the membrane, and it provided the best results. The amino acid was enantioselectively transported against the flow of various metal ions and especially the alkali ions of Na^+ , K^+ , and Rb^+ . The flux and optical resolution ratio of the amino acid depends heavily on the concentration ratio and concentration (initial concentration of the crown ether is made C^0 and the anion initial concentration is made X^0) of the two carriers in the membrane (Figure 1). The following results were obtained:

- (1) The flux is decided by the smaller value between C^0 and X^0 .
- (2) The greater the C^0/X^0 , the greater the optical resolution ratio.
- (3) The greater the C^0 , the greater the optical resolution ratio when $C^0 = X^0$.

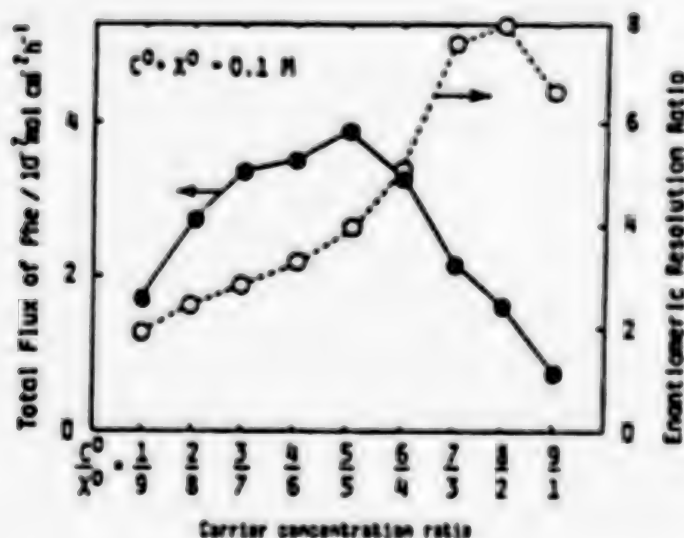


Figure 1. Dependence of the Total Flux of Phenylalanine (\bullet) and the Enantiomeric Resolution Ratio (\circ) on the Concentration Ratio of Chiral Crown Ether $\mathbf{1}$ (C^0) to DNNSA (X^0) in the Differential Countertransport When C^0+X^0 Was Kept Constant

These experimental results can be sufficiently explained by the theoretical equations based on studies on the transport mechanism.

Separation of Alcohol/Water Mixtures Through Ionized Membranes

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[Article by Shuzo Yamashita, Research Association for Basic Polymer Technology, Kuraray Co., Ltd.]

[Text] **Abstract:** We have investigated hydrophilic membranes for pervaporation through which water permeates preferentially and found that the membranes obtained from salts of polysaccharide, polyacrylic acid, and polystyrenesulfonic acid have high membrane performances in the separation of ethanol/water mixtures. In this report, we will reveal mainly the membrane performances of ionized polysaccharide membranes prepared from cellulose, chitosan, and alginic acid. The reason the high membrane performances cannot be explained only by the fact that the affinity of the membranes toward water is increased by ionization but will be explained well by the conformation change and the mobility of polysaccharide molecules. The conformation change and the mobility of polysaccharide molecules were investigated using CP/MAS-¹³C NMR.

In the research and development of high efficiency polymer separation membranes in the Project of Basic Technology for Future Industries, we used various polymer materials and conducted research on the water selective transmission type osmotic vaporization membranes in the water/ethanol separation. As a result, we found that the ionized membranes of polysaccharide, polyacrylic acid, and polystyrene sulfonic acid gave a superior performance. In this report, we will mainly relate the membrane performance and separation mechanism of polysaccharide system ionized membranes consisting of cellulose, chitosan, and alginic acid (Figure 1) and will report in detail on the ionized membranes of the polyacrylic acid and polystyrene sulfonic acid at another time.

Regarding the cellulose membrane, the separation factor improved from 6.7 to 194 but the permeation speed was 3.4 kg/m²h and 6.53 kg/m²h and a great difference was not recognized when salt consisting of polyhydric metals and polyhydric anions was added in the 65 wt% ethanol/water mixture of the liquid. It is believed that the remarkable enlargement of the separation factor is due to the fact that the affinity of the membrane for water is increased by ionization of a specific salt, the cellulose molecules adopt a

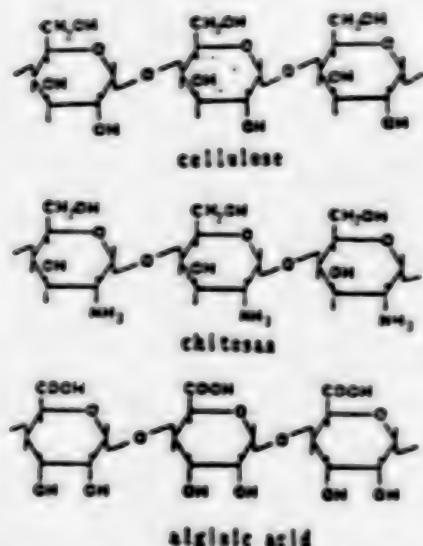


Figure 1. Chemical Structures of Polysaccharides

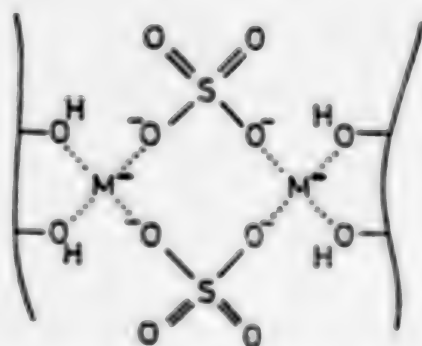


Figure 2. Ionization and Crosslinking of Cellulose by Metal Salt

suitable conformation for the separation, the molecular order fine holes becoming the passage for the transmission molecules shrunk, the permeation of ethanol molecules larger than the water molecules were controlled, and the fine holes were maintained by crosslinking (Figure 2). Therefore, since metallic ions--with a greater electronegativity in which the coordination bonding force with the oxygen in the cellulose molecules became strong--could easily ionize the cellulose, the increase of the separation factor was conspicuous in the metallic ions with an equivalent valent number generated from polyhydric anion salts. Since a suitable conformation for separation could not be maintained by crosslinking with salt consisting of a monovalent anion, the improvement of the separation factor could not be practically realized even in metallic ions with a large electronegativity. Besides this, various experimental results were available that suggested the conformation change of the cellulose molecules played a part in increasing the separation factor. Moreover, the conformation change of the cellulose molecules has been confirmed from the shifting of the glycoside chain C₁ and C₄ carbons in the CP/MAS-13C NMR to the high magnetic side by ionization (Figure 3).

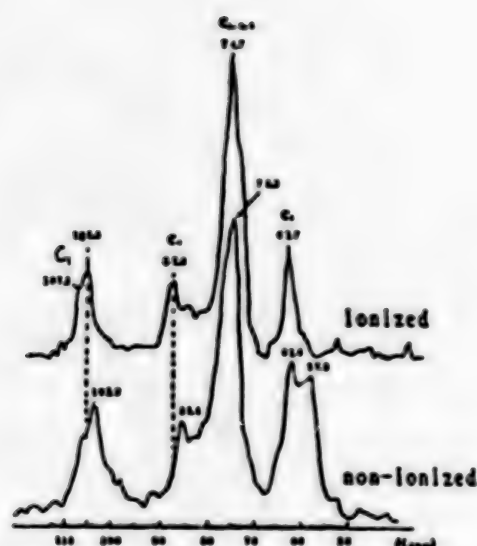


Figure 3. Solid State CP/MAS- ^{12}C NMR Spectra of Cellulose

By the way, salt must always be made to coexist in the original solution to maintain the high performance of the cellulose membrane. However, since this was not practical, chitosan and the alginic acid that could be considered as having greater interaction with ions than that of cellulose and indicating high performance without adding salt to the original solution after the ionizing treatment of the membrane were selected and studied as the membrane materials.

When chitosan was ionized with metallic salt, the salt consisting of polyhydric metals and polyhydric anions as in the cellulose membrane was effective in improving the separation factor and when metallic salt did not exist in the original solution, the metallic ions that are coordination bonded to chitosan gradually flowed out and the separation factor started to decline. Therefore, as a result of studying the chitosan membrane ionized by the polyhydric acid, we discovered that the separation factor could be highly maintained ($>1,000$) even when polyhydric acid was not added to the original solution. Moreover, when it was ionized by the polyhydric acid with a large dissociation constant, the separation factor of the chitosan membrane tended to become greater. However, when comparing the geometrical isomers and for example the fumaric acid and maleic acid, the separation factor was bigger when ionizing the fumaric acid with a small dissociation constant. It can be considered that this was because it was easy to maintain a suitable conformation for separation in the fumaric acid in which the crosslinking among molecules was possible. Moreover, results that could be related to the fine structure of the chitosan molecules were also available. For example, the permeation speed of water is approximately fixed when the ionized percentage of chitosan increases and the separation factor increases as the permeation of the ethanol molecules larger than that of the water molecules is considerably controlled (Figure 4).

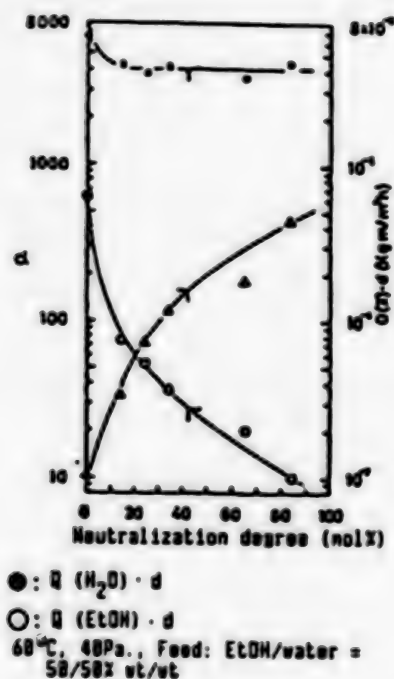


Figure 4. Relationships Between Membrane Performance and Neutralization Degree (Acid: H_2SO_4)

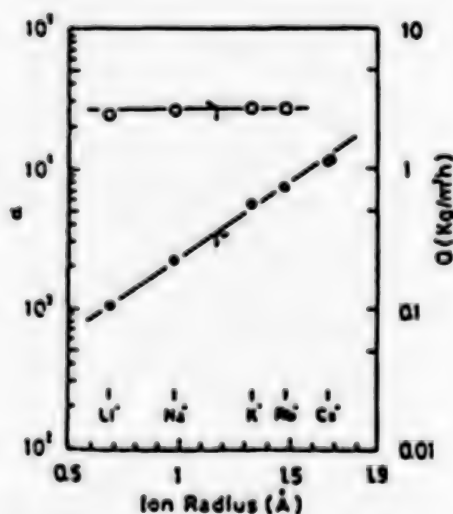


Figure 5. Effect of Counter Ion on Performance of Alginate Membrane
 60°C, 40 Pa., Feed: EtOH/water = 90/10 wt/wt

When the alginic acid is ionized with the alkali metal elements, the separation factor regardless of the metallic salt is approximately fixed ($>1,000$) and the permeation speed is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (Figure 5). Since the conformation of chitosan is not controlled by the ion type and is approximately fixed, it is reasoned that a separation factor does not

exist in the ion type. However, since the affinity between the alginic acid salt and water is $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$, the permeation speed cannot be explained by the affinity between the membrane and water. Therefore, upon investigating the activity of the alginic acid salt by the spin-lattice relaxation time available from the solid NMR, it was reasoned that the reason the permeation speed became the greatest in the Cs salt among the alkali salts of the alginic acid was because the activity of the molecules was greater in comparison to other metals due to the fact that the activity became greater in the order of $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ (Figure 6).

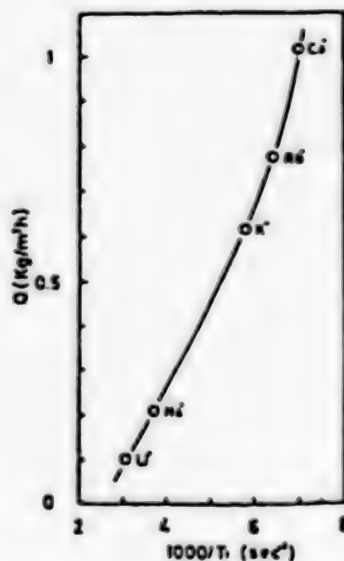


Figure 6. Relationship Between $100/T_1$ and Q
 T_1 : spin-lattice relaxation time obtained
 from solid state CP/MAS- ^{13}C NMR

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R&D Trends in Photoactive Materials

430638031 Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 143-145

[Article by Shigeo Tazuke, Research Laboratory Resources Utilization, Tokyo Institute of Technology]

[Text] **Abstract:** Since 1985, a new project entitled "Photoactive Materials" has been organized within the framework of R&D Project of Basic Technology for Future Industries sponsored by MITI. Outline of this long-term (8 years) project is reviewed with reference to the general trends of material research relevant to high-density and high-speed information storage and processing. Aiming at establishment of basic technology relevant to superhigh density recording, high resolution display, and optical switching, two lines of research are now underway, one is on the development of photochromic materials and their application to multiplex recording (Research Institute for Polymers and Textiles, Hitachi Chemical Co., Matsushita Electric Industries Co.) and another is on photochemical hole burning (PHB) system (Electrotechnical Laboratory, Toray Industries, Inc., Mitsubishi Electric Corp., Sony Corp.). Research progress during the first 3 years (phase I) including the first success of PHB at liquid nitrogen temperature is summarized.

1. Material Chemistry of the Light Age

The use of light in place of conventional electricity for transfer, conversion, recording, and regeneration of information is theoretically advantageous in areas such as stability of the information density, processing speed and memory capacity system. We are already moving into the light age as seen in the large capacity optical communication and optical disks. However, materials that are used in optical communications with the exception of the light-receptor are passive materials and it is believed that materials actively responding to light will be in demand in the future. Even in optical recording, the present materials used are not those that respond to light, but those which respond to the generation of heat caused by the absorption of light. Light as an information medium essentially can handle an enormous amount of information and is diverse in comparison to electricity. Outstanding information density is achievable when a combination of various information such as wavelength, intensity,

polarization, phase, and mode is used. The light must be utilized in the photo mode (electron transition and the succeeding optical reaction) and not in the thermal mode. The material that responds to the photon mode is indeed the material that becomes the nucleus in the light age. Expectations are placed in optical recording as the utilization field of optical response materials in the near and distant future. It may be a field where various technologies control light with light in the future.

2. Outline of the New Project Entitled "Photoreactive Materials" Within the Framework of the Project of Basic Technology for Future Industries Sponsored by MITI

Two national research institutes (Electrotechnical Laboratory and Research Institute for Polymers and Textiles of MITI) and five civilian enterprises (Toray Industries, Inc., Mitsubishi Electric Corp., Sony Corp., Hitachi Chemical Co., Ltd., and Matsushita Electric Industrial Co., Ltd.) have been participating in this project that was started under the schedule of 8 years from the latter part of 1985. The purpose of the research was to reversibly change the structure and assembly state of molecules by the light action and develop an optical response material usable in the ultrahigh density information recording, etc. Moreover, it is expected that the results obtained will accelerate the development of ultralarge capacity memory devices capable of coping with the ultralarge computers, ultrasmall disk devices, etc., and it will contribute to a high-speed optical arithmetic processing technology utilizing the optical switch and the high resolution display technology. To be specific, the development is being promoted by two research paths.

The first is to develop a photochromic molecule and apply it to the multiple optical recording material. Photochromic means the phenomenon which discolors by the energy of light and restores it to the former state by the light irradiation of a different heat and wavelength. In a large sense, it means the phenomenon in general in which not only the color tone but the physical properties (molecular form, polarity, electrical properties, optical properties, mechanical properties) change widely. The attempt to utilize the photochromic phenomenon for recording is a suggestion from the olden days and things such as the improvement of reversibility, spontaneous control of the color erasing process, sensitivity improvement, and improvement of long wavelength sensitivity, must be achieved. However, even if such improvements are made, there is little technological potential in replacing the optical recording material of the thermal mode that is now nearing the stage of practical use. The biggest advantage of the photon mode lies in the fact that the diversity of light can be utilized and that it aims toward the application of the photochromic molecule in the depth/direction-multiple recording and wavelength multiple recording. The recording density of optical recording is about 60 Mb/cm², i.e., about 10 times that of magnetic recording without multiplexing and this advantage is further promoted by multiplexing. Basic research such as the multilayer integration technology of the coloring matter system and coloring matter with a narrow band absorption spectrum, the stabilization technology by the compartmentalization of amplexus, may become the main research subjects during the 3 years of phase I.

The other research path is to develop a photochemical hole-burning material. This principle was pointed out by the USSR in 1974, demonstrated by IBM in 1976, and is a dream material that has a recording density surpassing all of the present recording materials in principle. When various pigments exist in the medium, the pigment-medium undergoes various interactions and provides many energy levels and the absorption spectrum becomes wide. An equilibrium develops among the various energy levels in this condition and when only coloring matter in a specific level reacts by irradiating monochromatic light of a certain wavelength, the wide spectrum form is not changed and the entire strength only slightly decreases. Although the spectrum form may be wide in a condition where the molecule action stops, the various energy levels constituting the spectrum are isolated and become independent. In other words, when the coloring matter of a specific level is resolved, a hole can be bored in the spectrum in that portion only. A large wavelength multiplicity that is not comparable with the multiplicity above mentioned in the first research path becomes possible under this principle. A system having a recording capacity of more than 10^4 Mb/cm² has also been demonstrated in the experiment room, however, it has the following problems:

(1) How can a matrix be created with its molecular activity frozen at higher temperature? Experiments on PHB are generally carried out in the neighborhood of the liquid He temperature. However, it is desirable for the practical material to work at a temperature as high as possible. When the temperature of PHB which was once recorded at low temperature is raised, the hole width expands but also reversibly becomes narrow to a certain degree when dropped to low temperature again. Therefore, both factors of the temperature for recording and reading and the temperature for enabling record storage are important. Various polymers and sol-gel type glasses are used as matrices, however, the most basic part of what sort of molecular exercise mode is obstructing the PHB phenomenon has not yet been clarified. The temperature characteristics also differ by the combination of the coloring matter (phthalocyanine, quinizarin, etc.) matrices. First of all, the goal is to be able to record and store at the temperature of liquid nitrogen. The measuring method has also not been established regarding the fine exercise of the polymer main and side chains in extremely low temperature and this has become an extremely important basic research topic.

(2) The factor that determines the homogeneous width and heterogeneous width of the spectrum, i.e., the expansion of the entire spectrum (heterogeneous width) is great and the means to obtain a sharp hole with a narrow homogeneous width is also still in the basic research stage.

(3) There are also problems that must be solved when it comes to practical use, for example part of the record disappears when reading. However, priority must be given to basic analysis for understanding the PHB phenomenon itself at the present stage. At the same time, the number of color matters seen in the PHB phenomenon is few and it should be decided beforehand to increase the experimental cases from the standpoint of synthetic chemistry. If the multiple photochromic materials are to become

materials for the next generation, the PHB materials should be called materials for the generation after next, and when the PHB materials are developed, a huge recording density will be available and the effects on the information industry will be immeasurable. Although the memory materials are the present focus, this research should be grasped from the viewpoint of a comprehensive technological development which reversibly causes the physical property change of materials by light. When the results are successful the static memory materials will provide a basis for the material which can dynamically control light with light.

3. Other Topics

(1) Photochromatic Materials

1) Stabilization of spiropyran group

The spiropyran is the most well-known photochromic molecule but the stability of its repetition characteristic and coloring condition is not good. The stability and the wear resistance of the coloring body (merocyanine) have been remarkably improved by the amplexus of the γ -cyclodextrin derivative. The phenomenon of the coloring body becoming stabilized is also recognized when preparing and fixing the J-aggregate. It has also been shown by molecular assembly technology that there is much room for improvement of the photochromic characteristics together with improvement of the molecular structure itself.

2) Basis of integration technology and multiple recording

It is necessary to narrow the spectrum width of the coloring base for wavelength multiple recording. The absorption band of merocyanine becomes sharp by allowing the preparation of the J-aggregate and stacking is possible by making it into an LB membrane. The possibility exists of allowing light reaction by separating the absorption bands of the many types of the photochromic compounds.

3) Various read-out methods

Optical rotation, circular dichromism, and optical anisotropy as alternative read-out methods are promising, in addition to light absorption. Together with amplifying and research the form change of the cholesteric liquid crystal and optical activity polymer with the photochemical reaction as the trigger, fading at read-out can be prevented.

(2) PHB Materials

1) Optical multirecording

We have succeeded in writing more than 100 pieces of information between the wavelength width of 8 nm with polyvinyl alcohol as the matrix and quinizarin the host.

2) Realization of high temperature

The hole width became wide but the temperature characteristics were considerably improved in the ionic polyphrin/polyvinyl alcohol system and it has been shown that the hole generation was possible by the liquid nitrogen temperature. Items 1) and 2) are presently the superior data in the world.

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Photochromic Liquid Crystal Effects

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[Article by Kunihiro Ichimura, Research Institute for Polymers and Textiles]

[Text] **Abstract:** Two liquid crystalline systems showing reversible optical property changes are presented. Dissolution of chiral azobenzene derivatives in nematic liquid crystals afforded chiral nematic liquid crystals which exhibited photo-induced reversible phase transition between cholesteric and isotropic phases based on the photochromism of the azobenzenes. The photochromism can be followed by monitoring the transmittance of linearly polarized light which does not induce any photoreaction. The reversible change of optical rotation was observed when photochromic compounds were dissolved in a solid thin film of cholesteric polymers.

1. Introduction

There are many points that should be solved in applying the photochromic materials to the reversible optical memory and it is necessary to clarify the reaction field effects. We are exerting efforts to systematically comprehend these effects by separating them into effects from the reaction field and to the reaction field. It can be said that the liquid crystal indicating discontinuous phase changes is an extremely interesting reaction field also from these two viewpoints. The liquid crystal effect to the thermal return reaction speed has been reported as the photochromism effect from the reaction field and several liquid crystal changes accompanying the photochromism have been reported as effects to the reaction field.¹

Photochromic materials reversibly change the various chemical and physical characteristics in addition to the absorption spectrum change. There lies the possibility of utilizing the change of the optical characteristics in which a wavelength does not exist for the nondestructive read-out of the latter. When fixing one's eyes on the optical anisotropy of the liquid crystal, the destruction of the optical information in case of read-out can be prevented by detecting the phase change of the liquid crystal caused by the photochromism by polarization. Explanations will be given here on the

system in which the photochromism in the cholesteric liquid phase of the low molecules and polymers is detected as transmittance and optical rotation changes of the linearly polarized light.

2. Photochemical Reversible Phase Change of Chiral Nematic Liquid Crystal^{2,3}

The chiral nematic liquid crystal phase which has dissolved the chiral azobenzene in a nematic liquid crystal is expected to change from the cholesteric liquid crystal phase to the nematic liquid crystal phase and further to the isotropic phase with the photoisomerization of the azobenzene. Therefore, various chiral azobenzenes have been synthesized. The cyclohexyl carboxylic acid phenylester system mixed crystal liquid (1) and the benzoic acid phenylester system liquid crystal (2) were used as the nematic crystal liquids. The pitch when mixing 5 wt% of the chiral trans-azobenzene has been arranged in Table 1 [not reproduced].

These chiral nematic liquid crystals form a cell when sandwiched between glass plates which have undergone rubbing orientation treatment. When the cell is irradiated with ultraviolet radiation, the pitch expands along with the photoisomerization reaction from trans- to cis-azobenzene, then further changes to the isotropic phase. When visible light was irradiated on this and the isomerization to the trans configuration was made, it returned again to a phase having a value close to the former pitch. The change to the isotropic phase is facilitated in the cis body as the amount of azobenzene increases. The cholesteric and isotropic phase changes can be monitored as the transmittance of the He-Ne laser beam under the perpendicular intersecting Nicol prism changes. The reversible transmittance change of the He-Ne laser for the system adding 15 wt% of the chiral azobenzene to liquid crystal 1 is shown in Figure 1. Information is nondestructively read-out by the He-Ne laser beam differing from the wavelength causing photochromism in this system.

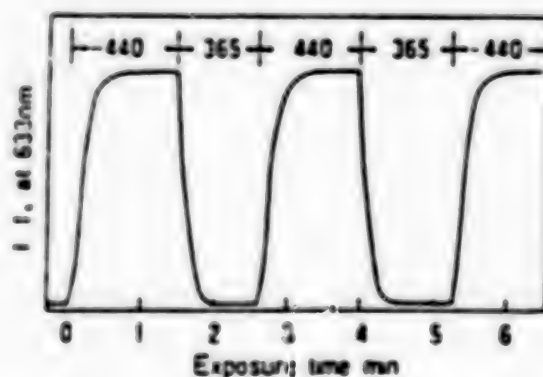


Figure 1. Reversible Change of Transmittance of Polarized He-Ne Laser Light Through a Chiral Nematic LC Cell Containing a Chiral Azobenzene on Alternative Exposure to UV and Light

There is a delay in the liquid crystal phase change following the photoisomerization reaction and it is greatly dependent on the type and

temperature of the liquid crystal. The response of the mixed liquid crystal (1) is extremely slow. However, the response speed increases with the rise of temperature and greatly increases when nearing the phase transition temperature. This cannot be explained by the viscosity effect of the liquid crystal only. On the other hand, it has been discovered that the absorption spectrum of azobenzene in the liquid crystal changes depending on the concentration. This is due to the association of azobenzene. It may be that the response was expedited due to the forming of the monomeric azobenzene as it reached high temperature. Tabu and others have reported that the nematic liquid crystal which has mixed azobenzene reversibly changes into the isotropic phase with photoisomerization⁴ and have also shown that it is a physical S/N amplifying system. The system mentioned here has also shown a similar behavior and it can be perceived as an amplifying system.

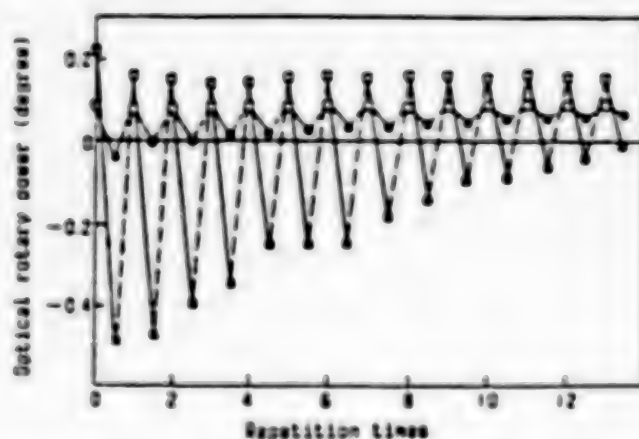


Figure 2. Reversible Change of Optical Rotatory Power of Polyglutamate Thin Films Containing a Spirocyan of 1 mole% (\circ) and 4 mole% (\bullet) on Alternative Illumination With UV (—) and VIS Light (---)

3. Photochromism in the Polymer Cholesteric Liquid Phase Field

The lack of definition caused by the flow property of the liquid crystal becomes the essential problem in the abovementioned reversible photosensitive materials. Thereupon, attention was turned to the solid-state polymer cholesteric liquid crystal and the optical changes accompanying photochromism were investigated. When dissolving spirocyan (3) in poly(ester L-glutamate) (PBLG), making it a membrane of less than 10 μm and irradiating ultraviolet rays and visible light alternately on it, an optical rotation change accompanying the photochromism was observed.⁸ The $\alpha_D = 1^\circ$ in the thickness of 1 μm is equivalent to $[\alpha]_D = 100,000^\circ$ (concentration: 1 g/cm³; cell thickness: 10 cm) and is abnormally large as an ordinary chiral organic compound. An optical rotation change accompanying similar photochromism was also seen when using azobenzene. The optical rotation change in such a PBLG thin membrane necessitates the forming of a cholesteric phase. Therefore, such an optical change is not recognized in a polymer matrix having a chiral base like the

poly(methylmethacrylate). It seems that this phenomenon is a universal phenomenon to photochromism in the cholesteric phase. The photoisomerization of azobenzene dissolving in the low molecular cholesteric liquid crystal induces the reversible change of the cholesteric pitch.⁶ On the other hand, it is known that the coloring matter molecules in the cholesteric liquid phase indicate the circular dichroism (LCICD) in the wavelength range. Therefore, it is presumed that the optical rotation change accompanying photochromism in PBLG is caused by the pitch change of the cholesteric polymer or by the LCICD change.

Investigations were made on the system dissolving various photochromic molecules in the cholesteric monomer to clarify this fact.^{7,8} For example, the cholesteric band shifts reversibly when isomerization of the azobenzene was made in the monomer condition. In contrast to this, it becomes a cholesteric polymer when the photopolymerization initiation agent is added, the cholesteric band becomes fixed and the pitch does not change. The thin membrane indicated an optical rotation change accompanying the photochromism. Therefore, it can be concluded that the optical rotation change accompanying the photochromism is not caused by the pitch change.

The optical rotary dispersion induced by the cholesteric liquid crystal phase was also recognized in the cholesteric band range together with its recognition in the absorption maximum wavelength range of the fulgide coloring matter. This phenomenon was also observed in the azobenzene, which was considered rather common. Therefore, since the optical rotation change is detectable in any wavelength range separated from the wavelength causing the photochromism, these systems can also follow the nondestructive read-out principle.

4. Conclusion

The results mentioned here concern the pursuing of photochromism in the crystal liquid field under a linearly polarized light and circularly polarized light. It is necessary to solve several problem points in utilizing them for the optical recording body. In other words, the problem points that must be solved are the response speed and resolution, especially in cases when using the low molecule crystal liquid system becomes the problem. Since a photochromic photosensitive system that shows high resolution can be devised even when using a fluid crystal liquid, we expect to make reference to it in the future. It may be that extra efforts must be exerted on the response speed.

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20158/9365

Multifrequency Optical Memory System

43063803n Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 151-153

[Article by Junichi Hibino, Central Research Laboratories, Matsushita Electric Industrial Co., Ltd.]

[Text] **Abstract:** Long-chain spiropyrans, SP1822, and SP1801, can be formed into J aggregates in LB films. Two compounds show different behaviors. SP1822 LB film forms with heat and UV irradiation and SP1801 film forms with stearic acid or stearyl alcohol. Both J aggregates have very sharp absorption bands and are much more stable than monomer forms.

We can propose a multifrequency optical memory system, which is constructed with the photochromic compounds having the different sharp-absorption bands and is recorded on a spot with different laser lights, as shown in Figure 1.

1. Introduction

Emphasis will be placed on matters such as reloadability with the photon mode, and realization of large capacity by multiplexing, in the development aspects of future optical recording mediums. The photochromic materials have attracted attention from these aspects. The organic photochromic material among the photochromic materials has the characteristics of controlling the optical reaction by the combination of the skeleton and substituent.

Photochromic materials are made into thin membranes by using the LB method and are capable of controlling the optical reaction and thermal stabilization of materials. It has been discovered that when the long-chain spiropyrans (SP1822, SP1801) are made into LB membranes, the photomerocyanine (PMC) of the coloring body forms J-aggregates and drastically improves the thermal stability. The absorption peak itself also becomes sharp. If this phenomenon is controllable, the recording of the multibit information per single spot will become possible by stacking the photochromic materials having different wavelength absorption, and an ultrahigh density optical recording can be achieved (Figure 1).¹

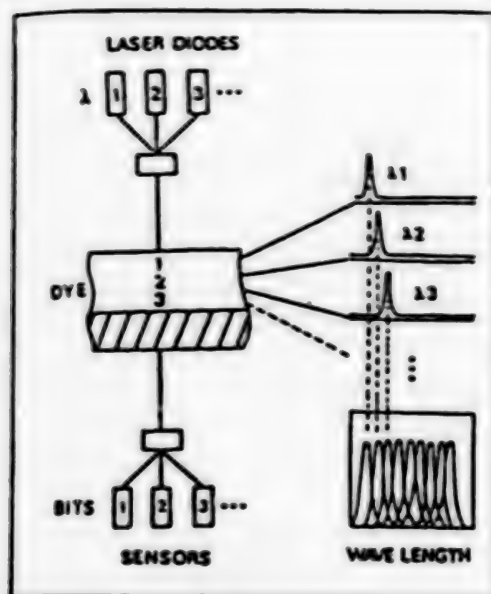


Figure 1. Concept of Multifrequency Optical Memory

2. J-Aggregate of SP1822³

The SP1822 forms a superior condensation membrane by its mixture with octadecane (HC 18). This LB membrane changes into photomerocyanine (PMC) when irradiating ultraviolet rays. However, similarly in a solution and in a polymer matrix, it thermally fades when shelved in a dark place at room temperature and can be restored to its former SP state.

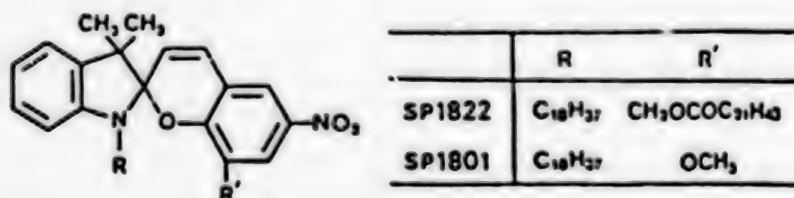


Figure 2. Chemical Structures of SP1822 and SP1801

The absorption spectrum changes when this SP1822 LB membrane is irradiated with ultraviolet radiation at the 35°C atmosphere (Figure 3). It was confirmed that J-aggregates (J-PMC) were formed by the absorption shifting to red and the fluorescence inversely shifting to blue in comparison to PMC. The thermal stability of J-PMC was improved by about 10⁴ times in comparison to that of PMC. Moreover, since the exact same absorption spectrum was seen also in the monomolecular membrane, it was discovered that the number of associated molecules was 6 to 8 by means of the two-dimensional expansion dipole model (Figure 4).

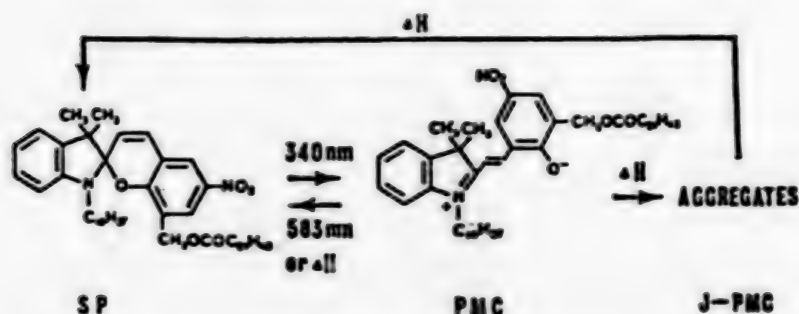


Figure 3. Photochromic Reaction of SP1822

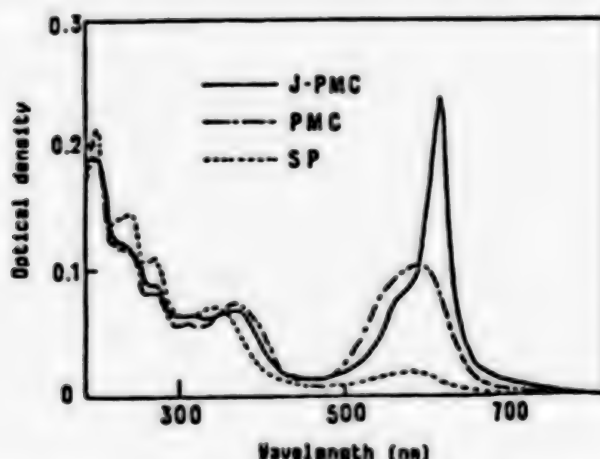


Figure 4. Absorption Spectra of SP1822/HCl8

3. J-Aggregate of SP1801³

The coloring body of SP1801 is stable in a polar solvent and on the air-water interface. Reflecting the behavior of the air-gas interface at the initial state, the coloring body of the LB membrane mixed with HC 18 is also stable, however, the period to reduce it by half is short and it is restored to the SP state in 30 minutes. Since the SP1801 was susceptible to the polarity effect of the field, the mixed membrane with stearin (SA) was studied to change the polarity in the LB membrane. As a result, the SP1801: SA = 1: 1 LB membrane peak spontaneously rose sharply at room temperature when shelved in a dark place and an aggregate was formed (Figure 5). Since this aggregate in comparison to PMC had a small Stokes shift though the absorption of 2 maximum was the same, it was after all considered to be a J-aggregate (Figure 6). Moreover, this J-aggregate is about 10^4 times more stable when compared with the PMC state. In addition, since it is also formed in a monomolecular layer, it can be considered caused by the interaction among molecules and not between layers. The J-aggregate was also observed in the mixed membrane with stearyl alcohol but it could not be observed in the barium stearate and methyl stearate.

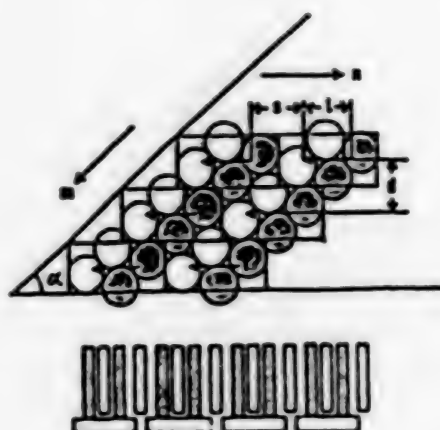


Figure 5. Arrangements of SP1822 and HCl8 Molecules

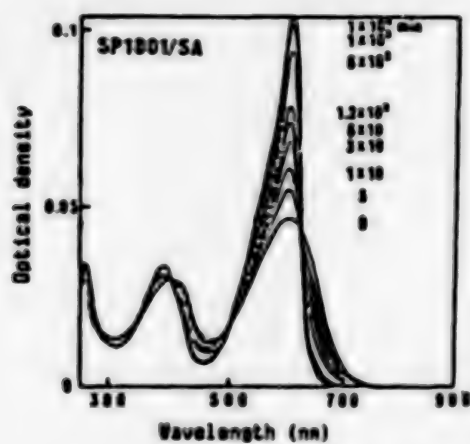


Figure 6. Absorption Spectra of SP1801/SA

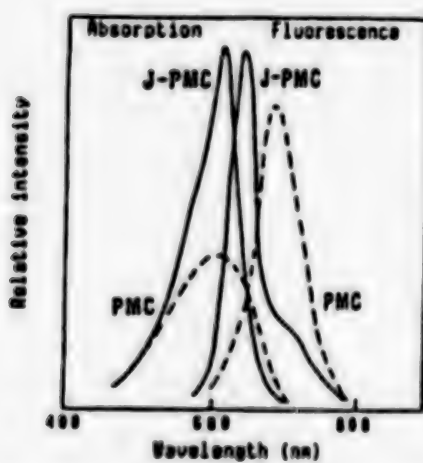


Figure 7. Absorption and Fluorescence Spectra of SP1801/SA

4. Conclusion

We have shown here two J-aggregate forming photochromic materials called SP1822 and SP1801. In contrast to the SP1822 forming an aggregate by the interaction among the PMCs, the SP1801 does not form an aggregate independently. It forms an aggregate for the first time by controlling the interaction with the matrix materials.

The J-aggregate forming of the photochromic materials is an extremely important phenomenon in both the high densification and recording life increase of the optical memory. It may be said that a step forward has been taken in realizing an ultrahigh density optical multmemory by controlling two types of different J-aggregates.

This research has been conducted as a link in the "Research and Development of Optical Reaction Materials" based on the Project of Basic Technology for Future Industries sponsored by the Agency of Industrial Science and Technology, MITI.

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20158/9365

Photochemical Hole-Burning Materials: Characteristics of Dye Molecules, Matrices

43063803o Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88
pp 154-156

[Article by Toshiro Tani, Electrotechnical Laboratory]

[Text] **Abstract:** Our recent studies will be described on the basic properties of photochemical hole burning of organic dye molecules, 1,4-dihydroxyanthraquinone (DAQ) and its related molecules, doped in a variety of organic or inorganic glassy matrices. From the results on the molecules in which the number and the position of hydroxyl groups are changed or one or both of the hydroxyl groups are substituted, the electronic and structural conditions on DAQ and related molecules for the formation of persistent holes are discussed. As for the matrix effect of DAQ/glassy polymer systems, we found a strong correlation between the saturated hole width and the density of electric dipoles in the polymer matrices. Hence we try to deduce the possible mechanism of hole broadening, which surely originate from the irreversible nature of amorphous solids. Characteristics of the PHB materials to be endowed as future data storage are critically reviewed.

1. Introduction

The project on the research and development of the optical reaction materials was started in late November 1985 as the first new theme in the Project of Basic Technology for Future Industries sponsored by MITI. The research on photochemical hole-burning (PHB) materials among the research on optical reaction materials was limited to a small number of research workers and research agencies abroad although the research was active and innovative. The Ibaraki Communication Research Institute of NTT began operations as an actual operation agency in Japan in addition to our Electrotechnical Laboratory and it was indeed a start made under the next generation state. The total of four agencies, three consignment companies, and one national research institute, are to participate in this research and development of PHB materials and our Electrotechnical Laboratory will take on the task of clarifying the basic characteristics of the PHB materials.

The hole-burning phenomenon, itself a well-known phenomenon in the quantum electronics field and the hole-burning phenomenon mentioned here, is one of the site-selective optical phenomenon optically generating in a solid cooled to a low temperature (normally less than 10 K). The essential characteristic lies in the fact that the hole is everlasting. For example, when coloring matter molecules are dissolved in ethanol and are frozen with liquid helium, a colored glass with the coloring matter molecularly dispersed is created. When a monochromatic light like the laser beam is irradiated on such a system, there is decreased absorptivity at selected sites in a narrow wavelength range only and it sometimes looks like bored sharp holes in a photoabsorption spectrum. This is the PHB phenomenon and it was discovered for the first time in 1974 by two groups, the Gorokhovskii group and another group from the USSR. In addition to its original bright future as a spectroscopic means of high resolution to study the dynamic processes of phase relaxation of the excited state, the idea by the San Jose Research Institute group of IBM centered around G. Castro on the possibility of creating a high density multifrequency optical memory by applying this phenomenon has come to attract wide attention.

A PHB hole is practically permanent and the point where each hole is formed independently is important. Since more than 10^3 holes can be opened in a single absorption band, the high densification of 10^3 times is possible by wavelength multiplexing when 1 and 0 bits of the digital information are made to correspond with the presence of holes. Therefore, it is theoretically possible to make it 10^{11} bit/cm² or more against the upper limit of the recording density of the present optical disk system being made about 10^8 bit/cm². Of course, the status quo is still far from realizing such a high density optical memory. Much of the preceding research is centered around basic science and there are many technological problems that should be solved. Among the many breakthroughs that must be made, those concerning the recording material itself are most important. It is felt that feasibility as a memory must be confirmed in the first place. To achieve this, the research promotion method that differs considerably in character from the conventional material developments is important. It should be designated as constructing a new material science within the boundary between high-level basic sciences such as photochemistry, organic chemistry, inorganic chemistry, polymer chemistry, physical chemistry, solid-state physics, cryogenics, quantum electronics, and advanced technology fields such as lasers, optical recording technology, and organic electronic materials. From this, it is wise to take up the PHB materials as the new theme in MITI's Project of Basic Technology for Future Industries which has deep significance as an ideal national project.

2. PHB Materials

Both the optical active coloring matter molecules (color center) and the supporting solid-state mediums are necessary for the formation of everlasting holes. Since it is said that the cross-talk among the data-bit holes basically occurs when there is interaction among the coloring matter molecules, it will do to lower the concentration in order to avoid this. However, it would be better to have many PHB activity centers that can be

utilized to realize the abovementioned multiplex in a domain similar to that of the bit area of the present optical disk. There are many cases where there is rather great interaction among (guests) in case of organic coloring matter molecules and often about 10^{-3} mol/l becomes the upper limit of molecular dispersion in the known PHB system. Technology for enlarging the solubility and dispersion in the medium without condensation and technology for controlling the molecular absorption degree is necessary when putting it to practical use as a recording material.

It goes without saying that the characteristics demanded in the recording materials are dependent on the adopted read and write methods and systems. However, those characteristics that can be considered basically preferable are listed as follows:

- (1) The multiple (band width/hole width of absorption band) is great.
- (2) High efficiency and high-speed PHB reaction mechanism.
- (3) Stability in write and read-out operations.
- (4) Rise and improvement of record deposit, holding temperature, and operating temperature.

A considerably high level has been observed for each of these characteristics, however, under certain conditions. For example, the system of about 10^3 is normally observed when concerning multiplexing only. However, the time on the order of seconds is generally necessary for forming and detecting holes. This is because there is no threshold value in the reaction for generating holes and a sufficiently strong light cannot be used for read-out as many of the presently known material systems have the single photon process mechanism. Of course, it would not be proper to discuss the rights and wrongs of the existing material system because PHB research is presently at the basic stage as far as comprehension of the phenomenon is concerned. It is not directly targeting application for research materials. The phenomenon itself is simple and the governing factors of the hole spectrum are more complicated than they appear. We must understand as soon as possible the respective microscopic roles of the central activity and each medium, and accumulate the knowledge and examples that are indispensable for material design. We will introduce here the present status of the basic research on the characteristics of the coloring matter molecules and amorphous mediums that we have conducted at our laboratory based on such a policy and will discuss the problem points and future development based on these results.

2.1 Color matter molecules

The quinizarin (1,4-dihydroxyanthraquinone, DAQ) of the organic coloring matter molecule is preferably used for the prototype of the PHB active center. This molecule has a structure of one each of the hydroxyl group (OH-) that is the electron donative functional group adhering to the 1 and 4 positions of the π -electron skeleton of the anthraquinone. These two pro-

(oxygen atom). It is said that the reaction mechanism of PHB may be a confirmation change in which this intramolecular hydrogen bond is disconnected in the excited state and the hydrogen bond changes over the polarity part of the molecule constituting the medium. Our experiment results do not deny this hypothesis. From the results of the series of derivatives changing the numbers and positions of the OH- group, it has been discovered that the structure in which the two functional groups, one group each, respectively, in the 1 and 4 positions, was essential in manifesting the PHB phenomenon with this molecule. The hole does not appear when there is only one functional group in the 1 position and the OH- groups added in the 2, 3, 6, and 7 positions did not contribute to the reaction. Based on this fact, it has been discovered from the results of the derivatives in which other functional groups (for example, amino group, NH-) with a different electron donative property and form factor were substituted in place of the OH- group, that it differed from the conventional hypothesis and could be considered that both the 2OH- group in the 1 and 4 positions were simultaneously participating in the optical product at least.

2.2 Mediums

We are trying to widely systematize the medium effect by glass mediums regardless of whether it is of the organic system or inorganic system. It is a well known fact that the amorphous materials characterized by its nonequilibrium state were discovered rather recently. The PHB materials, on the other hand, have advantages of having better control over a microscopic structure and thereby capable of expecting an increase in multiplicity. Studies have been widely done up to now covering glasses made of organic polar low molecules with DAQ as the probe material to polymer glasses and further to α -SiO₂, that form a three-dimensional network by inorganic polymer. Above all, an important clue to the origin of the saturated hole width has been discovered from measuring the medium effect by the series of polymers of the polyolefin system. When considering the medium effect, it is possible to classify the bond between the active molecule and the medium (guest-host), i.e., the interaction between the electron and lattice, by turning attention to its active range. The interaction among the electric dipoles is the main interaction in case of the abovementioned DAQ/polymer glass, the structure relaxation (two-level systems, TLSs) peculiar to amorphous is spectrum diffused through this interaction and it suggests the possibility of appearing differently from the dynamic phase relaxation. In our report on this matter, we expect to relate the discussion centered around this idea on the origin of the hold spectrum and TLSs in the glass medium.

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Photochemical Hole-Burning of Anthraquinone Derivatives in Acrylic Polymers

43063803p Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 157-159

[Article by Noriaki Tsuda and Motomu Yoshimura, General Research Laboratory, Mitsubishi Electric Corp.]

[Text] Abstract: We have carried out this study in order to develop the multiplexed optical memory in the wavelength dimension and high density optical memory by use of photochemical hole burning (PHB). At the first step, we investigated the PHB reactions of the anthraquinone-derivatives in the acrylic polymers in order to elucidate the characteristics required for the PHB materials, that is, guest and host molecules which can produce multiplexed PHB holes at high density.

As a result, we have found out the new PHB material which can produce more than 100 multiple holes in only 8 nm wavelength intervals. What this means is that it is now possible to store information at as high a density as 10^{10} bits/cm².

We have also shown that it will be possible to use a semiconductor laser as a light source to cause the PHB reaction, which will be profitable for the optical memory system.

1. Introduction

The miniaturization, large capacity, and high processing speed of information processing devices have come into demand with the remarkable progress made in the high-level information processing society. The realization of a high density and large capacity memory becomes extremely important for satisfying these demands. There is the optical memory as a memory capable of realizing a high density. However, the 10^8 bit/cm² is the limit for the optical memory according to the spot diameter ($\sim 1 \mu\text{m}$) of the laser beam used. There is the multiple recording of information into a single recording spot as a method of overcoming this threshold value. There is the method using photochemical hole-burning (PHB) which performs multiple recording in the wavelength dimension as its representative method. PHB is a reaction that opens holes in the absorption spectrum of molecules. The absorption spectrum (ω_1) of the guest molecule dissolved in

the host molecule is the sum of the homogeneous absorption spectrum (ω_H) of various wavelength positions conforming to the various energy states caused by the interaction difference with the host molecule. When the laser beam with the wavelength of γ_n is irradiated in the frozen state of energy, the molecule having an absorption of γ_n only photochemically reacts, the absorption γ_n decreases and holes are generated in the spectrum. When the laser beam wavelength is changed, a hole is made in each wavelength position and the hole corresponds to the information of 0 and 1, the multiple recording in the wavelength dimension becomes possible (Figure 1). The multiplicity (ω_I/ω_H) of more than 10^3 and the recording density of more than 10^{12} bit/cm² are theoretically possible. We have developed a new PHB material, generated more than 100 holes in the wavelength of 8 nm, achieved the take-out of a signal equivalent to 10 billion bit/cm² and demonstrated the possibility of a high density recording by PHB.

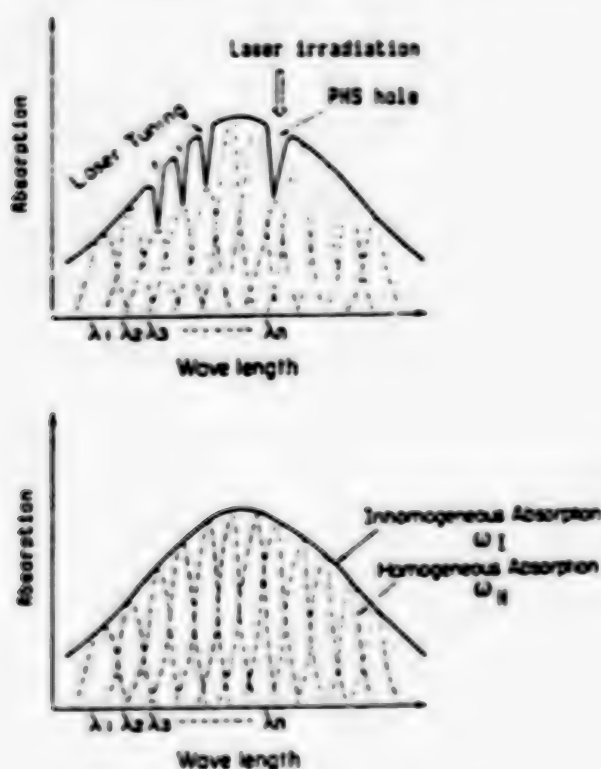


Figure 1. Principle of PHB

2. Experiments

2.1 PHB material system

The following guest molecules and host molecules are used.

Guest molecules: 1,4-dihydroxyanthraquinone (DAQ); 4-amino-2,6-bis-(4-butylphenoxy)-1,5-dihydroxyanthraquinone (ABDAQ); 4,11-diamino-5,10-dihydro-2-(3-octyloxy) propyl-3-thioxonaphto [2,3-f] isoindoline-1,5,10-trion (DAN).

Host molecule: Poly-2-hydroxyethyl methacrylate (PHEMA); polymethyl methacrylate (PMMA).

3. Results

3.1 DAQ/PHEMA system (formation of high density holes)

It is important that each hole is mutually independent and there are many numbers of component spectral (ω_s) for multiple recording with PHB. The side holes were held down, the efficient generation of resonance holes was possible, and the independence of each hole was promoted in this system (Figure 2). Moreover, the absorption spectrum of DAQ was made into a long wavelength by about 100 nm by using PHEMA as the host rather than using PMMA. It is considered that the component spectral number of DAQ increased. This is likely due to the fact that PHEMA has two polar groups. More than 100 holes were formed at the interval of 0.08 nm in the wavelength of 8 nm of the absorption wavelength of 572 to 580 nm by the abovementioned characteristics (Figure 3). As a result, it is equivalent to recording the signal of 10 billion bit/cm² by the multiple of 100.

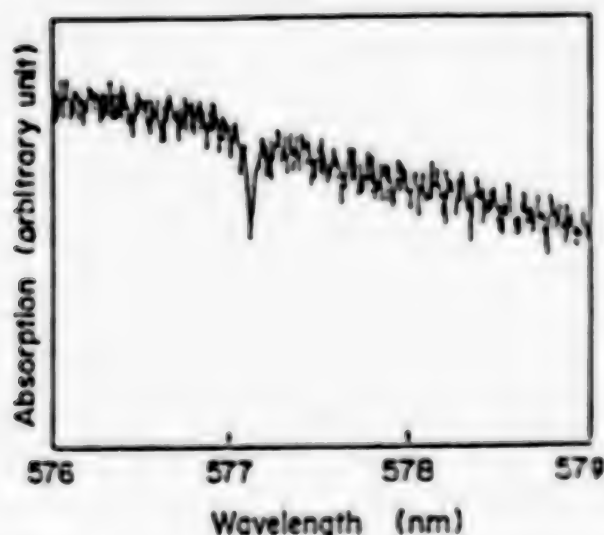


Figure 2. Typical Hole Profile in DAQ/PHEMA

3.2 ABDAQ/PMMA system (interaction among holes)

It has also been shown from the results of this system that the independence among the holes is important when conducting multiple recording. The generation rate of side holes becomes high in this system and the preceding holes were destroyed by the following holes unless the space between the holes was separated at more than 0.5 nm. Therefore, only two to three holes could be made in 1 nm and the multiplicity became one-fourth of the DAQ/PHEMA system.

This seems to be affected by the three-dimensional structure of ABDAQ.

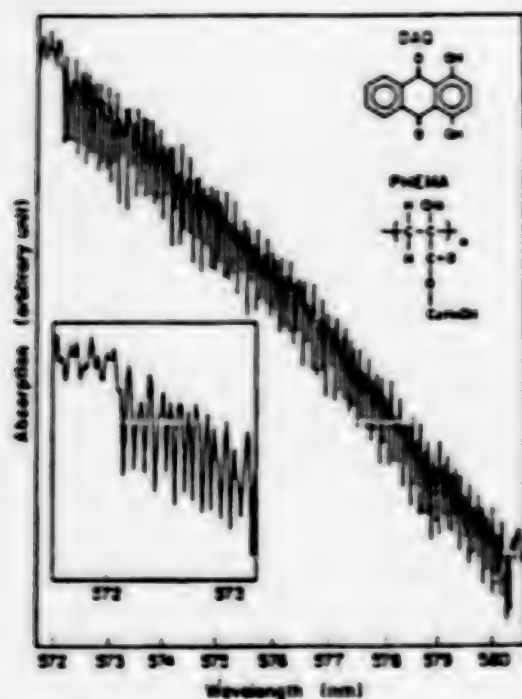


Figure 3. High Density Multiple Hole Formation in DAQ/PMMA

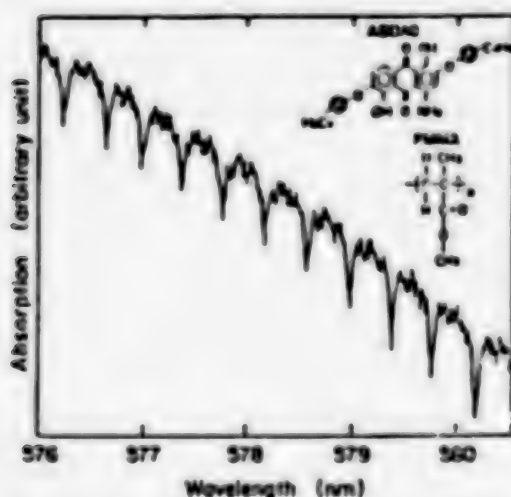


Figure 4. Multiple Hole Formation in ABDAQ/PMMA

3.3 DAN/PMMA system (long wavelength realization of hole generation)

It is desirable from designing the system to use the semiconductor laser when conducting PHB multiple recording. The absorption region has been made of a longer wavelength region up to the neighborhood of 800 nm by the electronic properties of the guest molecular substituent in this system and holes were stably formed by the laser beam of 750 nm (Figure 5). This indicates the possibility of generating holes by the semiconductor laser.

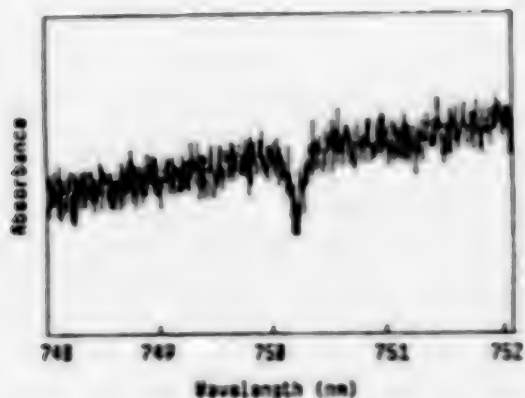


Figure 5. Hole Formation at Longer Wave Region

4. Conclusion

The possibility of high density recording by PHB has been demonstrated by the abovementioned results and information has been obtained on the molecular design guideline of PHB materials making this possible. A structure in which the number of interaction modes with the guest molecules becomes great is important for the host molecules. It is important to have a structure where the phonon interaction of the host becomes small without losing the PHB activity. Moreover, it has been clarified that the generation of a stable hole by the semiconductor laser is possible by selecting the substituent of the guest molecule according to the electronic properties.

We extend our hearty thanks to Department Chief Takashi Nakayama and Mitsuo Maeda for their guidance to us in conducting this research.

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Next-Generation Fine Ceramics Technology R&D Project

43063804a Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 161-163

[Article by Akio Nagahiro, Engineering Research Association for High-Performance Ceramics: "'Jisedai' R&D Project on Fine Ceramics and Material Technology"]

[Text] **Abstract:** The "jisedai" [next-generation] fine ceramics R&D project is peculiar in that it is entirely directed toward the development of material science and technology. It is just reaching the end of its second phase. During the first and second phases, improvements in each individual technology, shown in Table 1, were attained, which will be reported at the relevant sessions and with posters. Some cooperation work was carried out for clarification of the relationship between material powder characteristics and the sinterability of sintered body properties as well as for the proposal of a ceramic parts-designing standard manual based upon systematic compilation of strength measurement data under varied modes of stress. They will also be reported in the sessions hereafter.

In the third phase, which starts this coming April, studies on the development of new high-toughness materials and surface strengthening techniques will begin. The aim of this project for systematizing the material technology is steadily being approached, but worldwide cooperation is desired to gain the essential value of success taking account of the wide extent of the technology.

1. Characteristics of Research and Development of Jisedai [Next-Generation] Fine Ceramics

The research and development of fine ceramics under the Jisedai Industrial Foundation Technological R&D System was undertaken as basic research aimed at establishing the position of fine ceramics as future high-load machine part materials superior in energy efficiency, taking advantage of the high-temperature strength, anticorrosion and wear resistance characteristics of ceramics that surpass those of metallic materials. This goal of purely technological development, rather than development of specific apparatuses and systems, is unprecedented in the history of national research under the jurisdiction of the Agency of Industrial Science and Technology and of the

various government research projects in the United States and Europe. The first phase (3 years) and the second phase (4 years) have been completed, and the third phase will begin in April this year. Research within this project is presently being conducted through the close cooperation of the 6 national research organizations and 15 private companies comprising the Engineering Research Association, with the assistance of national universities and some commissioned organizations. The trend of total research expenditure for each year from the start of the project in 1981 up to FY 1987, as indicated in Figure 1, has shown a steady increase. Until FY 1985, the appropriation was taken from the general account budget of the Agency of Industrial Science and Technology, but then, in FY 1986 the source was partially switched to the power resources special account budget, and in FY 1987 it was totally taken from the latter source.

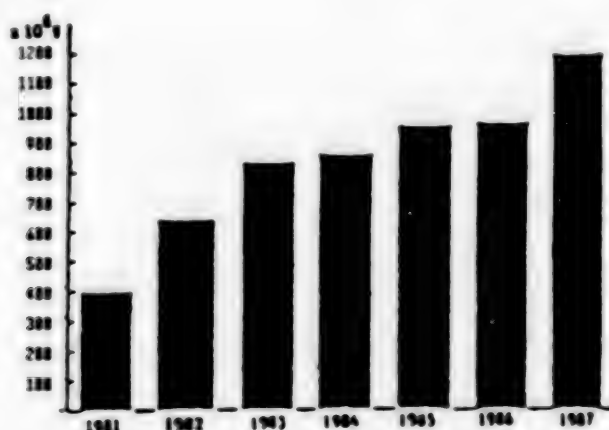


Figure 1. Yearly National Budget for the Project

2. Progress and Results of First and Second Phases

To establish the position of structural fine ceramics as an industrial material, it is necessary drastically to improve their reliability in resisting destruction. Increasing the tenacity of the material itself is a task to be tackled in the third phase. The first and second phases, silicon nitride and silicon carbide were selected as conventional monolithic sintered bodies for study from the standpoint of elucidating the material technology; elements relating to the reliability of their material physical properties and capacities were exhaustively elicited from two aspects--manufacturing process and use technology--and the measuring and evaluating techniques absolutely necessary to link both aspects correctly were determined. Efforts were exerted not only to improve and develop those elements but also to systematize them as material technology. The details of the research are shown in Table 1. To test development results, three types of materials (high strength, highly anticorrosive, and high-precision wear-resistant materials) were decided on based on the qualities of silicon nitride and silicon carbide. An overall evaluation was made. We sought to realize target capacity values (Table 2) in the shape of JIS test pieces during the first phase, and in models of simple shapes, as exemplified in Figure 2, during the second phase, and to conduct spin tests

Table 1. Assignment of Themes in the Second Phase

| Individual Item | Organization in charge |
|---------------------------------------|---|
| 1. Process Technology | |
| (1) Process-developing fundamentals | |
| 1) Process-process-Science | Government Industrial Research Laboratory, Nagoya |
| 2) Forming by explosion | National Chemical Laboratory |
| (2) Material powder synthesis | |
| 1) Silicon nitride | Engineering Research Association for HPC |
| 2) Silicon carbide | Engineering Research Association for HPC |
| (3) Forming and sintering | |
| 1) High strength materials | Engineering Research Association for HPC |
| 2) High corrosion-resistant materials | Engineering Research Association for HPC |
| 3) High wear-resistant materials | Engineering Research Association for HPC |
| (4) Machining and joining | |
| 1) Machining | Mechanical Engineering Laboratory Engineering Research Association for HPC |
| 2) Joining | Engineering Research Association for HPC |
| 2. Evaluation Technology | |
| (1) Property evaluation | |
| 1) Material powder | Government Industrial Research Laboratory, Nagoya |
| 2) Sintered pieces | Government Industrial Research Laboratory, Nagoya, Osaka, and Kyushu |
| (2) Reliability evaluation | |
| 1) Mechanism of fracture | National Institute for Research of Inorganic Materials |
| 2) Proof-testing technique | Engineering Research Association for HPC |
| 3) NDE technology | Engineering Research Association for HPC |

[continued]

[Continuation of Table 1]

| Individual item | Organization in charge |
|--|--|
| 3. Application Technology | |
| (1) Designing technology | |
| 1) Structure analysis and designing criteria | Engineering Research Association for HPC |
| 2) Structural element test methods | Engineering Research Association for HPC |
| (2) Testing of developed models | |
| 1) High strength materials | Engineering Research Association for HPC |
| 2) High corrosion resistant materials | Engineering Research Association for HPC |
| 3) High wear resistant materials | Engineering Research Association for HPC |

Table 2. Objective for R&D of High-Performance Ceramics

| Material | Target value |
|-----------------------------------|--|
| High strength materials | <p>(1) After it is kept at over 1,200°C for 1,000 hr in air, it shall be tested at 1,200°C in air and satisfy the following values:</p> <p>1) Tensile strength (mean value) $\bar{\sigma}$: over 30 kg/mm² (294 MPa)</p> <p>2) Reliability (Weibull modulus) m: over 20</p> <p>(2) It shall be tested by 1,000 hr creep test at 1,200°C in air and satisfy the following value: Creep rupture strength σ: over 10 kg/mm² (98 MPa)</p> |
| High corrosion resistant material | <p>(1) After it is kept at over 1,300°C for 1,000 hr in air, it shall be tested at 1,300°C in air and satisfy the following values:</p> <p>1) Tensile strength (mean value) $\bar{\sigma}$: over 20 kg/mm² (196 MPa)</p> <p>2) Reliability (Weibull modulus) m: over 20</p> <p>3) Corrosion resistance (weight gain in oxidation): less than 1 mg/cm²)</p> |
| High wear resistant materials | <p>(1) After it is kept at 800°C for 1,000 hr in air, it shall be tested at 800°C in air and satisfy the following values:</p> <p>1) Tensile strength (mean value) $\bar{\sigma}$: over 50 kg/mm² (490 MPa)</p> |

[continued]

[Continuation of Table 2]

| Material | Target value |
|----------|---|
| | 2) Reliability (Weibull modulus) m : over 22 |
| | (2) As to the following items, it shall be tested at the room temperature and satisfy the following values: |
| | 1) Wear resistance (specific wear amount): less than $10 \text{ mm}^3/\text{kg}\cdot\text{mm}$ |
| | 2) Precision (surface roughness) R_{max} : less than $2 \text{ }\mu\text{m}$ |

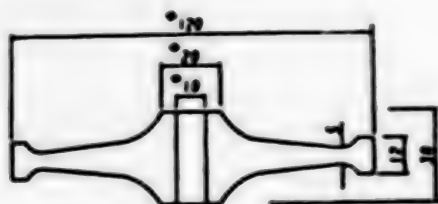


Figure 2. First Stage Model for High-Strength Materials

and other functional tests for the models. As reported in the previous open symposium, both the raw material powders and sintered goods concerned in the small-scale research in the first phase attained their target capacities and achieved the world's best quality.

During the second phase, the results achieved in individual element techniques, shown in Table 1, were studied in particular from the viewpoint of material science. All of this is reported in today's morning and afternoon sessions (24 March) and is displayed on posters. Noteworthy joint-work results were achieved concerning the relationship between the physical properties of raw material powders and their moldability and sinterability and the physical properties of sintered bodies, the organized collection of test data on fracture strength under various stress conditions, and the proposal of ceramics parts design standards based on these data. These will be announced in a lecture today.

3. Third Phase and Subsequent Plans

In the third phase, the general results of development technology in reference to the overall plan will be tested using complex-shaped models closely resembling practical components. With the introduction of a special account budget, a ceramic turbine for coal gasification composite power generation" was chosen as the target. It is important as next-generation research in order to establish systematic knowledge of all material techniques that offer the most effective technical guidance while coping with problems concerning the fabrication and use of components for this gas turbine. In the middle of FY 1987, research activities began in

order to tackle such tasks as developing new high-tenacity materials, including research to improve the capacities of conventional materials, developing surface strengthening techniques and establishing destruction criteria and design standards for mechanical shocks, because it was anticipated that the materials used in the past for such research and development and their capacities would be inadequate for the environments in which the materials required for the gas turbine would be used. Furthermore, in this phase, technical cooperation in manufacturing and data accumulation concerning evaluation and application will receive even greater emphasis.

4. Expectations of the Path Opened for Advancing Material Technology

It must be specifically mentioned that next-generation research is being conducted for the sole purpose of technical development and is believed to have affected government research projects in Europe and America, as indicated by the fact that new material technology development projects, replacing earlier automotive gas turbine development projects, were started in the United States in 1983 and in Europe (the EC nations led by West Germany) in 1985. However, the scope of technologies related to next-generation research far exceeds that of this research, which itself has considerable technical scope and is progressing rapidly. Thus, coordination is indeed necessary to ensure the effectiveness of the next-generation research. As a side effect of the conduct of next-generation research, it has been mentioned that the practice of conversation and cooperation that developed among participating companies, which had been keen rivals until the start of the research and their exchange of information, has contributed to achieving better research results. It is hoped that the cooperation established in the development of ceramic materials technology will spread to become nationwide, even worldwide. I sincerely hope that this symposium will create an opportunity to achieve this end.

20108/9365

Development of High-Strength Silicon Nitride Ceramics

43063804b Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 168-170

[Article by Katsutoshi Komeya, Toshiba Corp.: "Development of High-Strength Silicon Nitride Ceramics by Microstructural Control"]

[Text] **Abstract:** Silicon nitride (Si_3N_4) is a highly refractory, lightweight engineering ceramic with a covalent chemical bond structure. Expected mechanical properties are based on optimum microstructure development which consists of the formation of strengthened texture and elimination of large flaws. Much effort to overcome this has been made in the fields of powder synthesis and consolidation process. In recent years, high-performance silicon nitride ceramics have been developed through high purity and fine grain of α type of silicon nitride powder formation, invention of yttria and alumina additives, and optimization of process parameters.

In this presentation, some of the above activities are reviewed.

1. Introduction

Silicon nitride (Si_3N_4) as a fine ceramic is characterized by heat resistance, wear resistance, and anticorrosion, having particularly high strength and thermal shock resistance. It is being developed for practical use mainly for vehicle parts and industrial machinery.

Its microstructure directly affects its strength characteristics because of its ceramic brittleness and its small K_{Ic} . The crystal control peculiar to ceramics is essential in the process flow from raw material to manufacture to evaluation.

2. Achievement of Compact, High-Strength Silicon Nitride

The compact sintering of silicon nitride began with the 1961 discovery of magnesia (MgO) additive in hot press sintering by Deeley, et al., and it progressed via the $\alpha\text{Si}_3\text{N}_4$ - MgO system of Lumby, et al., to the Si_3N_4 -rare earth oxide system of the author, et al. Meanwhile, the existence of what is now known as sialon--namely, the solid solution of aluminum (Al) and

oxygen (O) added to Si_3N_4 -- was discovered by Koyama, et al., Jack, et al., and Tsuge, et al., 19 years later. Today, silicon nitride ceramics are indeed complex because they contain two types of sialon: α and β .

Let us look at the example of the Si_3N_4 -yttria (Y_2O_3) system. Ordinarily, three elements, namely, these two and alumina (Al_2O_3), are used as starting substances for compacting. As a starting raw material, $\alpha\text{Si}_3\text{N}_4$ is used. When this three-element system is mixed, molded, and sintered, reaction between the silica (SiO_2) near the surface of Si_3N_4 or Si_3N_4 itself and the Y_2O_3 - Al_2O_3 system occurs to form a liquid phase. $\alpha\text{Si}_3\text{N}_4$ melts into this and is deposited as the β type. At this time, crystal grains grow in a needle (or long column) shape. High strength results as these needled crystals increase the tenacity of ceramics. So, the author named this "deposition-type fiber reinforced composite material." In a sintered body of this system, Al and O are partially solid-solved in Si_3N_4 , according to the amount of Al_2O_3 . When AlN is added to the above three-element system, α sialon crystals of Si-Y-Al-O-N are formed.

In conclusion, high strength can be achieved, by the development of application technology of the second and third phases in the grain boundary after the fine whiskers are controlled properly.

3. Achievement of High-Performance Silicon Nitride

As stated, the microstructure and the form of bonding affect the physical properties. The specifications required of silicon nitride ceramics differ according to purpose, but in regard to fine, high-strength ceramics, the requirement is that needle crystals with a large aspect ratio be dispersed minutely and evenly, that the grain boundary or the grain boundary phase firmly bond the grains, and that the grains be dispersed evenly and without pores. In this case, the physical properties of silicon nitride vary as a result of the addition of the solid solution of Al and O to the needle crystals and the state in which the grain boundary phase exists.

Achieving high quality, in essence, amounts to studying conditions to make organizational control of these possible and developing techniques to bring them as close to the ideal state as possible. Specifically, the techniques consist of powder technology, a homogenizing process, and, in particular, grain boundary engineering.

3.1 Silicon Nitride Powder

The synthesizing of $\alpha\text{-Si}_3\text{N}_4$ that is of high purity and in fine powder form is in demand. There are four different synthesizing methods: 1) direct nitriding of silicon (Si); 2) silica reduction nitriding; 3) imide decomposition; and 4) gas phase synthesis. The first three methods are mainly used. Regarding the second method, the author, et al., discovered the method of grading grains by adding Si_3N_4 powder to the $\text{SiO}_2 + \text{C}$ system and used it efficiently to develop high-strength silicon nitride. However, there is much that is not known about the powder. What is an ideal powder? Obtaining a uniform grain shape is detrimental to maximum density while assuming any shape of crystals reduces fluidity. In particular, Si_3N_4 is

complex, and the relationship between the state of oxygen, the surface condition, the internal structure and its applicability, and the sintered body characteristics remains to be elucidated in the future. In any case, synthesizing Si_3N_4 that is of high purity and in fine powder form has become possible, thus greatly contributing to the improvement of its sintered body characteristics.

3.2 Improvement of High-Temperature Strength by Grain Boundary Crystallization

As can be seen from Jack's correlational graph, high-melting-point compounds exist in the Si-Y-Al-O-N system grain boundary phase components. The heat resistance is high in proportion to how high the N/O ratio is. High strength is obtained at temperatures ranging from room temperature to about $1,200^\circ\text{C}$, using the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ or $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-AlN}$ system as the starting component, and by proceeding efficiently with sintering reaction and crystallizing the grain boundary phase. Furthermore, it has been confirmed that this crystallization progresses remarkably in the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-HfO}_2$ and ZrO_2 systems.

3.3 Improved Reliability Through Pore and Grain Control

In the powder treatment and molding process, the occurrence of defects, the residual large pores and the formation of agglomerates greatly affect sintered body characteristics, and in particular, strength deteriorates. Previously, it was the practice to depend on a hot press soon after development because of the difficulty of such process control. But now, the improved quality of the powder and the process techniques have made it possible to obtain products of superior quality even using atmospheric-pressure sintering. Furthermore, the elimination of defects has been achieved by HIP processing after atmospheric-pressure sintering, thus making more sophisticated applications possible.

3.4 Development of High-Temperature Strength Materials Utilizing HIP

As methods of HIP utilization, there are: 1) application to capsule HIP and atmospheric-pressure sintered bodies; and 2) capsule-free HIP. Through the first method, compacting without additives has become possible, and also, the abovementioned strength deterioration at high temperatures can be improved considerably. The second method consists of increasing high-temperature heat resistance in advance by grain boundary crystallization and using HIP to make up for inadequate compacting in the final stage. It is known that, in the case of a high-pressure gas atmosphere such as HIP, the presence of impurities in the sintering furnace lowers the melting point of the grain boundary phase. Thus, it is necessary to take countermeasures against this. In the research conducted on the theme of next-generation industrial foundation technology development, along with the qualitative improvement of raw material powders, many useful findings have been obtained from studies including microscopic observation.

4. Effect of High-Quality Achievement Using Crystal Control Technology

In applying ceramics to machine parts, there is a major obstacle: brittleness. The practical use of ceramics in this area has been difficult because of the lack of reliability of ceramics. As stated at the beginning, in ceramics, the microstructure governs the characteristics.

In silicon nitride ceramics, too, some practical components capable of withstanding dynamic environments have been created by the unpretentious but steady progress of the abovementioned crystal control technology. They include such items as the glow plug, the hot chamber, the turborotor, the rocker arm chip, and the bearing. Regarding the bearing, for instance, it has been confirmed that these ceramics show a similar life and form of fatigue to those of ball-bearing steel as a result of the elimination of microdefects and the development of high-tenacity textures. Thus, it has become possible to make effective use of the properties that characterize ceramics, such as heat resistance, wear resistance, anticorrosion, nonmagnetism, and light weight. The same can be said of the other items.

5. Conclusion

As has been indicated, silicon nitride ceramics technology has advanced steadily during the past several years. This is, of course, due largely to the advance not only of material development technology but also of the technologies of processing, joining, evaluation, and design.

Engineering ceramics, however, are still undeveloped, and it must not be forgotten that the important key to their future lies in the assurance of their quality and the level of their production costs.

Meanwhile, there are limits to the present materials. The right materials must be used for the right purposes, and the weaknesses of silicon nitride will be covered by other materials. But after all, what is wanted is ceramics with high tenacity. In this sense, it is important that, starting in FY 1987, improvement of the tenacity of materials and of their surfaces was added to the "element technology development for the coal gasification ceramic turbine" theme of the Next-Generation Industrial Basic Technology Research and Development System of the Ministry of International Trade and Industry.

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Influence of Powder Characteristics on Sinterability

43063804c Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 171-173

[Article by Shuzo Kanzaki, Government Industrial Research Institute, Nagoya: "Influence of Powder Characteristics on Sinterability and Microstructure Development"]

[Text] **Abstract:** In order to control the microstructure of ceramic bodies, fine-grained and high-purity starting powders are required. In addition, the correlation between the powder characteristics and its sinterability and the properties of the sintered bodies should be fully understood. During the first and second phases of this R&D project, synthetic technology for creating high purity and fine-grained silicon nitride powders, by means of 1) direct nitridation of metallic silicon, 2) carbothermal reduction of silica in nitrogen atmosphere, and 3) vapor phase reaction between silicon chloride and ammonia, has been developed. In this review, the sinterability of the silicon nitride powders developed and the properties of the sintered bodies will be discussed in relation to the powder characteristics.

1. Introduction

In the manufacture of structural ceramics, it is most important to produce sintered bodies that are fine-grained and homogeneous and have thoroughly controlled microstructures. The microstructure of sinterability are affected by such factors in the manufacturing process as molding and sintering, but the major factor is the characteristics of the starting material. To control the microstructure of a sintered body, therefore, it is necessary to grasp thoroughly the correlation between the characteristics and sinterability of the starting material and the characteristics of the sintered body.

In the research and development of fine ceramics, raw material synthesizing techniques have been studied and developed with a view to developing fine, high-purity silicon nitride and silicon carbide powders, and powders satisfying target values have been developed. Even if the individual characteristic factors of starting powders, such as grain size, grain shape, purity, agglutination, α -phase molar refraction, and oxygen content

in the case of silicon nitride, for instance, are grasped, there is the further question of the complex relationship among these factors when sintering takes place. Further, the type and amount of additives required for the fine sintering of silicon nitride and silicon carbide also act as factors. Therefore, the relationship between the starting powder and sinterability and sintered body characteristics has not yet qualitatively been fully clarified. So joint evaluation work is being conducted by those member companies of the Engineering Research Association that carry out raw material synthesizing or molding and sintering and by this institute in order to study the abovementioned correlation and determine the requirements of sintering starting powders in conjunction with the evaluation of the powders developed. Hereunder are some of the results gained concerning silicon nitride.

2. Sinterability of Silicon Nitride Powders Developed and Sintered Body Characteristics

Three types of powder synthesized by direct nitration (D), silica reduction (F), and the halogenated silicon method (R) were evaluated by hot-press, atmospheric-pressure sintering and other methods, using Y_2O_3 and Al_2O_3 as sintering additives. Table 1 shows the characteristic value of each powder, while Figure 1 shows the change in the shrinking rate of each powder at the time of sintering.

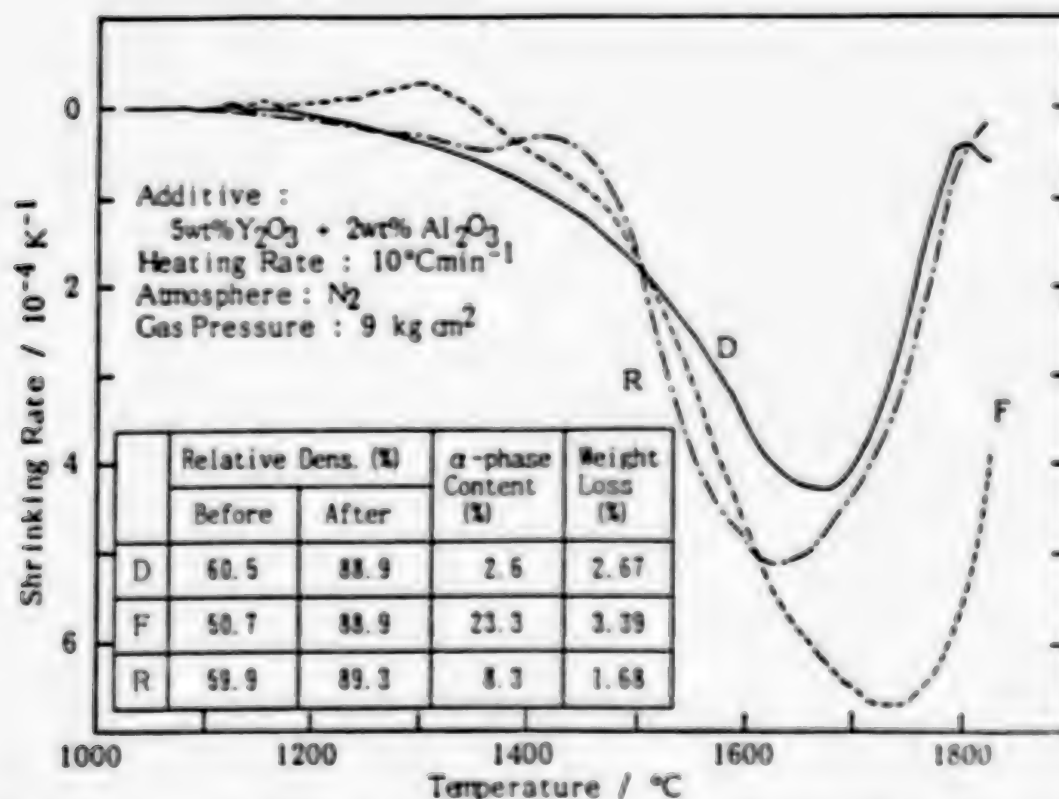


Figure 1. Shrinking Rate Vs. Temperature for Powders With SY-2A Additive

Table 1. Typical Properties of Si₃N₄ Powders

| Powder | S.S.A (m ² /g) | mean particle size(μm) | α-phase content (%) | Oxygen content (wt%) | Carbon content (wt%) | Metallic impurity (ppm) | | | |
|--------|------------------------------|-------------------------------|-----------------------------|----------------------------|----------------------------|-------------------------|-----|-----|-------|
| | | | | | | Fe | Ca | Al | Total |
| D | 22.0 | 0.50 | 92 | 1.3 | 0.25 | 29 | 23 | 54 | 178 |
| F | 13.1 | 0.75 | 99 | 2.6 | 0.71 | 68 | 100 | 390 | 636 |
| R | 8.6 | 0.90 | 97 | 0.8 | 0.13 | 16 | 2 | 18 | 167 |

All powders exhibit much the same density as a result of shrinkage when the temperature is raised, but the shrinkage behavior varies. D shrinks at a low temperature, but R shrinks suddenly in the vicinity of 1,500°C and shows a maximum shrinking rate at a lower temperature than D does. F, meanwhile, is on the higher temperature side of D and R in regard to both the temperature at which shrinkage starts and the temperature at which the shrinkage rate is at its maximum. D>R>F is the α-β transition rate at the time of heating. In D, the β-phase proportion increases with compacting, but in R, compacting progresses faster than β-transition at low temperatures, while F exhibits β-transition at 1,700°C or more. The relationship between sintering time and density at 1,700°C or more was D>R>F at 1,700°C, for instance, and D>F>R at 1,800°C. The crystal phases that form in sintered bodies after measuring temperature rise shrinkage are both β-silicon nitride and silicate (Y₂Si₂O₇), but crystal phases other than silicon nitride formed in the course of heating differ according to the type of powder. As for the microstructure of the sintered body, in D it consists of columnar grains, but in R it has a texture wherein abnormally elongated grains surround fine grains, and in F it has a texture that is intermediate between these.

As to the characteristic of each powder, D has a wide grain size distribution, R has uniform grain size but a low oxygen content, and F is composed of flock and has a high oxygen content. The above results and sintered body characteristics can be consolidated for the 5Y-2A additive group in conjunction with starting powder characteristics as follows:

1) Powder produced by a breakdown process such as direct nitriding contains fine grains, compacting starts at a low temperature, and at the same time α-β transition occurs. So, grains grow uniformly and compact sintered bodies are composed of fine columnar grains. Thus, it is highly sinterable and makes compact sintered bodies. Therefore, its strength at room temperature is high, but at high temperature this declines sharply.

2) In powder with a high oxygen content and composed of flock, compacting first starts in individual agglomerates and in the contact between agglomerates. Then, when the heating temperature is in the vicinity of the melting point of silica, the agglomerates break up as a result of the infiltration of the liquid phase into the interiors of the agglomerates and

its reaction, and at the same time, sudden α - β transition and the development of columnar grains are believed to occur. So, pores can hardly be eliminated and adequate compacting is difficult. But in the case of hot-press or other pressurized sintering, compacting is easy and β grains grow appropriately, so the high-temperature strength is indeed superior.

3) Powder produced by a buildup process such as the gas phase method has fine, uniformly shaped grains and therefore becomes compact at a low temperature, but if the oxygen content is low, the grains grow abnormally at the beginning of β -transition and subsequent compacting is hindered. Furthermore, such powder cannot be expected to have great strength at room or higher temperatures because the texture becomes nonuniform, even though its long columnar grains cross each other three-dimensionally. This indicates that if the oxygen content is low, sintering attended by transition cannot necessarily achieve a homogeneous sintered body texture in what started from uniform grain size and grain shape. However, the sinterability and microstructure can be improved by increasing the oxygen content or β grains, thereby facilitating β -transition.

In regard to sintered body characteristics, particularly high-temperature strength and fracture toughness, it is desirable that the sintered body texture be composed of suitably elongated columnar grains that cross each other three-dimensionally. To this end, it is necessary to control compacting acceleration and α - β -transition speed as far as high-purity powder is concerned. Thus, it appears that optimizing the grain form and oxygen content of powder is indeed important.

We shall next see the results of a study of the relationship between oxygen content and specific surface area, on the one hand, and sinterability and sintered body characteristics, on the other, with respect to powder R.

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Studies of Joining of Silicon Nitride Material

43063804d Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 174-176

[Article by Masaaki Honda, Engineering Research Association for High-Performance Ceramics, Sumitomo Electric Industries, Ltd.]

[Text] Abstract: The joining of silicon nitride (Si_3N_4) is a key technology essential to the development of high-performance ceramic applications. This report presents the progress of R&D activities concerning the joining of Si_3N_4 material at the Engineering Research Association of High Performance Ceramics. The improvement of bond strength at high temperatures has been investigated for joining $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$. A diffusion joining process using $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-SiO}_2$ ceramics as insert material was carried out. The multilayered metallizing process using Ti/Cu/Ag was effective for joining Si_3N_4 steel. In the joining process, a stress release layer is placed between multilayered metallized Si_3N_4 (formed by ion plating) and steel. These layers are heat treated without applying pressure. The Si_3N_4 /steel joint has a bending strength of 50 kg/mm^2 or more from room temperature to 400°C.

1. Importance of Joining Technology

Silicon nitride and silicon carbide are typical of the fine ceramics that are being actively developed and applied to high-strength and heat resistant members, anticorrosive members and high-precision and wear-resistant members, taking advantage of their superior characteristics. To make fine ceramics practical as highly reliable structural components, it is necessary to develop various related basic technologies. There are limits to finishing fine ceramics themselves as components having complex shapes or incorporating them into apparatuses and systems, because characteristically they are brittle and hardly workable materials. Much is expected of the development of methods of ceramic-to-ceramic and ceramic-to-metal joining as a basic technology to overcome these difficulties. Ceramic-to-ceramic joining is effective as a method to process components of complex shapes that are difficult to manufacture singly, while ceramic-to-metal joining makes possible applications utilizing the advantage of each through combination with metals that excel in toughness, machining,

heat conduction and electric conduction, thus contributing to expanding the applications of ceramics as structural components.

The author, et al., are developing element technology in regard to silicon nitride so that the technology of silicon nitride joining can be used for the structural components of a future ceramic gas turbine.

2. Ceramic-to-Ceramic Joining of Silicon Nitride

The conditions necessary for ceramic-to-ceramic joining of silicon nitride (Si_3N_4) include 1) that the joint have the characteristics of Si_3N_4 , the base material, and 2) that the joining method be applicable to complex shapes. An ideal method to join Si_3N_4 directly to Si_3N_4 without pressurizing is difficult to achieve because of the absence of Si_3N_4 reactivity and deformability at high temperatures. The author, et al., carried out a study in which they inserted into the joining interface a ceramic intermediate that reacts to the base material, increasing the joining area as much as possible and reducing welding pressure. The targets of technical development are 1) that the tensile strength at $1,200^\circ\text{C}$ be at least 80 percent of that of the base material, and 2) that the Weibull coefficient be at least 15. The evaluation method used is in accordance with the JIS four-point bending test.

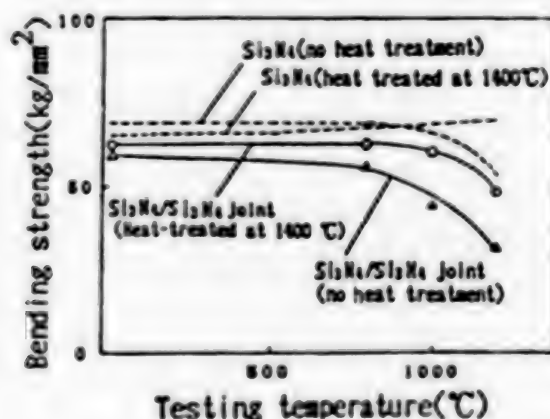


Figure 1. Bending Strength of Si_3N_4 and $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ Joint at Various Temperatures

Figure 1 shows the high-temperature strength of a ceramic-to-ceramic joined body of Si_3N_4 . An $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-SiO}_2$ ceramic was used as an intermediate. The high-temperature adhesive strength was improved by crystallizing the glass phase in the base material and on the joining interface after pressurized diffusion.

3. Joining of Silicon Nitride and Metal

When joining Si_3N_4 and a metal, it is necessary to control the reaction occurring on the joining interface as well as the thermal stress caused by the differential thermal expansion of Si_3N_4 and the metal. So, the author, et al., carried out a study in which they 1) formed on the surface of Si_3N_4 a metallized layer that easily adheres to a metal, 2) put a stress release

layer between the metallized Si_3N_4 base material and the metallic base material, and 3) used nonpressure joining to permit general-purpose utilization.

3.1 Discussion of Multilayer Metallizing

A metallized multilayer was formed on the surface of the Si_3N_4 base material by ion plating. Figure 2 shows the strength of the joining interface between the Ti/Cu/Ag metallized layer and the Si_3N_4 base material. A strength of more than 50 kg/mm^2 by heat treatment at $1,000^\circ\text{C}$ was confirmed. As a result of an X-ray diffraction of the joining interface, Ti_2Si_3 and TiN formed on the interface.

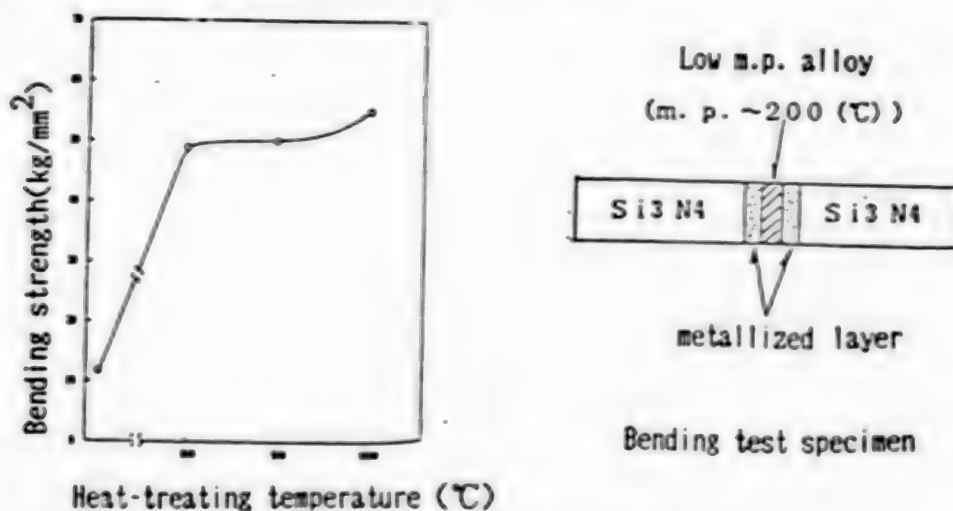


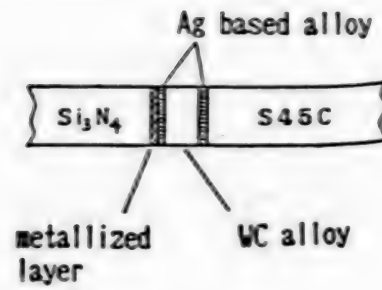
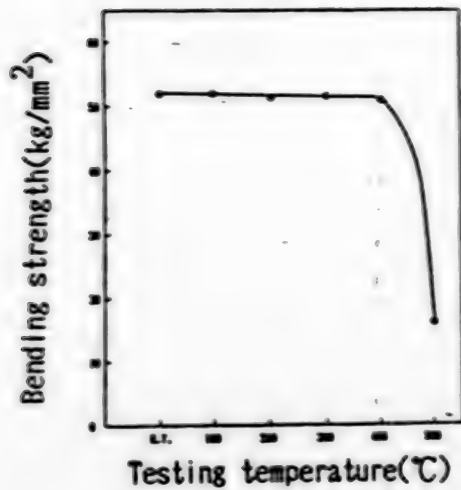
Figure 2. Strength of Si_3N_4 -to-Ti/Cu/Ag Metallizing

3.2 Joining of Silicon Nitride and Steel

A composite alloy material with almost the same thermal expansion coefficient of Si_3N_4 and high deformability was sandwiched as a thermal stress release layer between Si_3N_4 metallized using the abovementioned method and steel (S45C steel), and nonpressure joining was effected after heating in a vacuum. As indicated in Figure 3, adhesive strength of more than 50 kg/mm^2 was obtained in a JIS four-point bending test. Then, a study was made of the joining between Si_3N_4 and SCM steel, using test pieces with a joining area of $8 \times 8 \text{ mm}$. The results were as indicated in Figure 4. Adhesive strength of 36 kg/mm^2 was obtained as a result of use of Ni for the thermal stress release layer.

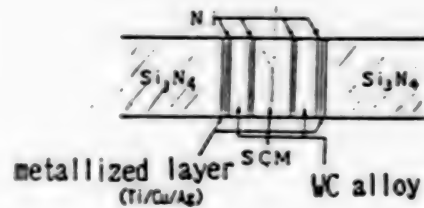
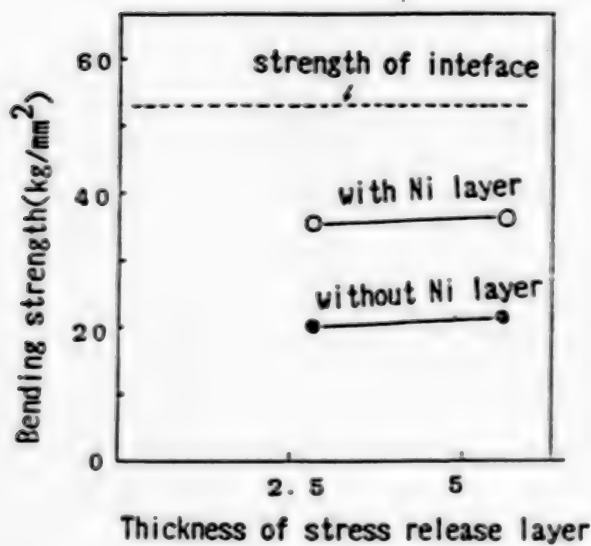
4. Future Direction of Development

For ceramic-to-ceramic joining of Si_3N_4 , a study will be made of a pressure load method that can meet the needs of complex-shaped components. For this joining, a study will also be made of thermal stress release measures including the conceptual designing of joint structures with a view to application to stationary blade models.



Bending test specimen

Figure 3. Strength of Si_3N_4 /SCM Steel Joint



Test specimen : 8 X 8 X 100 mm
 Bending test : upper span 26.7 mm
 lower span 80 mm

Figure 4. Strength of Si_3N_4 /SCM Steel Joint
 in Case of 8 x 8 mm Joining Area

Application Technology of Next-Generation Fine Ceramics

43063804e Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 177-179

[Article by Hiroshi Okuda, Japan Fine Ceramics Center: "Significance of Application Technology Development in Fine Ceramics Project"]

[Text] **Abstract:** The trend in application technology in structural ceramics is described herein. The substance of R&D for the application technology carried out in this project is as follows: 1) development of design methodology for ceramic parts; 2) evaluation of model parts for high strength, high corrosion-resistant, and high wear-resistant ceramics; and 3) research on fracture behavior of ceramics at high temperature. The significant and object of this R&D is explained. In order to construct design criteria, it is absolutely necessary to accumulate basic data related to the mechanical properties of ceramics. Tension, torsion, torsion/tension, bending and thermal shock tests as well as delayed fracture tests (static, dynamic, and thermal fatigue) for silicon nitride and silicon carbide ceramics were widely performed to gain reference data.

1. Introduction

It is not long since fine ceramics won public recognition as a structural material, but the development in this area in recent years has been impressive. Japan, in particular, which entered the area some time after the European countries and America, now ranks among the best in the world in the level of products and has greatly advanced in the research and development of basic technologies. Nevertheless, there are many problems to be resolved in order to be able to use brittle fine ceramics as structural materials, e.g., machine parts. Perhaps the greatest problem is to assure the reliability of their mechanical properties as materials and cut the product cost. So research and development is being conducted by many people in various countries. Research and development concerning next-generation fine ceramics consists of studying and developing technologies basic to their manufacture and application in coping with these problems. This article describes the details, meaning, and prospects of application technology include in the research and development of fine ceramics we are conducting under our next-generation program.

2. Details of Application Technology for Next-Generation Fine Ceramics

The application technology being developed for next-generation fine ceramics mainly concerns component design for fine ceramics to be used as structural materials and model component evaluation; it includes the setting of design standards, the analysis of strength factors and the collection of various types of strength data basic to designing.

In preparing design standards, the target is to set design standards for instantaneous fracture, static fatigue fracture, and dynamic fatigue fracture. The work consists in deciding on a simple evaluation method for instantaneous fracture, and having it reflected in the design standards and drafting design standards for time-dependent fracture. Also, the aim is to develop methods of analyzing heat conductivity and elastic stress that are more accurate than the conventional numerical analysis and to improve the accuracy of the technology to analyze the strength and reliability of fine ceramics relatively free from stress relaxation in parts with concentrated stress. This consists in developing the highly accurate analysis program that is required for the evaluation of the strength and reliability of ceramic components. Regarding strength factor analysis, we established a method to test instantaneous fracture under various stress conditions, acquired strength data, confirmed strength evaluation by Weibull statistics, verified fracture conditions under multiaxis stress, and developed a method to analyze the strength of fine ceramic members under stress change, with the object of clarifying the effects of various factors on instantaneous fracture strength and establishing a method of strength evaluation. We also developed various test methods to devise means for testing instantaneous fracture strength under various high-temperature atmospheres and conducted various analyses based on micro- and macro-observation of fractures to ascertain static and dynamic fatigue behavior at high temperatures. Also, we tested high-temperature fracture characteristics using large practical models.

3. Targets and Importance of Research and Development

Structural fine ceramics have many conceivable applications as heat resistant, anticorrosive, and wear-resistant materials, and they include oxides, carbides, nitrides, and borides, as well as composites of these and many other compounds. Already in practical use mainly are anticorrosive and wear-resistant components and stationary components not undergoing great stress at high temperatures. But considering not only present but also future applications of fine ceramics, a major target must be to make them practical as heat resistant components, notably as key components of a heat resistant apparatus, such as a high-temperature gas turbine, to be used at high temperatures and under great stress. If ceramics are achieved that can be used with high reliability under rigorous conditions, such as in a high-temperature gas turbine, able to withstand great stress and high-speed combustion gas at high temperature of more than 1,300°C, their applications will indeed be comprehensive.

The next-generation fine ceramics R&D project is aimed at studying the basic technology to develop silicon nitride, silicon carbide, and other

materials as ceramics that can meet these rigorous conditions, and at the same time, at developing application technologies and devising the design technology to apply fine ceramics as high-strength heat resistant, anticorrosive, and wear-resistant materials for such items as the ceramic gas turbine.

To this end, we are conducting research and development of application technology, as stated in the preceding section. As can be seen from these details, what is referred to here as application technology consists, at this point, not merely in developing the techniques necessary for application to the components of a certain apparatus, but in preparing the foundation for the design technology on which the application technology is to be based. First of all, to prepare general design standard and design guidelines concerning ceramics, it is important to accumulate data useful for various designs, and at the same time, to establish the element technologies necessary for designing specific apparatuses in the future. Of course, a future problem will be how to apply these basic design techniques to a more complex, more sophisticated apparatus, such as the ceramic gas turbine to be used for coal gasification power generation.

4. Outlook for Fine Ceramics Application Technology

Fine ceramics are brittle, low-tenacity materials. The measured values of their mechanical properties are so dispersed that, when designing apparatus components, it is a problem to decide what should be the minimum guaranteed values of strength, etc., or their safety factors. Also, when designing an apparatus, normally abundant material data are used for the design. However, reliable data on the fine ceramics of today are scarce. We must therefore begin by accumulating reliable data on the various strengths of these materials and other thermal and chemical data. But such data cannot be accumulated overnight, so it is important to prepare a design standard requirement for use in designing with few data. To this end, the minimum data necessary to design will be acquired, and at the same time, relatively simple design standards will be prepared by combining these data with stress analysis and statistics theory, etc. When these are ready, they must gradually be made complete through the acquisition of additional data and the development of theories so that they can finally be applied to the design of complex components.

Meanwhile, the establishment of test methods by which the properties of ceramics can be accurately evaluated is important to the progress of fine ceramics design technology. To establish test methods, the Standards Division of the Agency of Industrial Science and Technology is carrying out survey and research activities concerning fine ceramics standardization, and various measuring methods are being proposed by universities and research organizations; much can probably be expected of the results of these activities in the future. In our project, we are proceeding with the development of methods to test the various properties of fine ceramics and collecting data on fine ceramics, notably silicon nitride and silicon carbide. We are hoping to advance fine ceramics application technology in the future by enabling these accumulated data to be reflected in design technology.

5. Conclusion

To use fine ceramics as machine parts, related design technology must be established. But to achieve this end, many extremely different problems must be resolved, and unostentatious efforts are necessary to solve them. It is hoped that this project will help to resolve these problems.

20108/9365

Design Guide for Structural Ceramic Components

43063804f Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 180-183

[Article by Akihiko Suzuki, Ishikawajima-Harima Heavy Industries Co., Ltd.]

[Text] **Abstract:** A design guide is proposed to assure the safety and reliability of structural ceramic components which operate under mechanical and thermal loads. The guide is intended to keep the fracture probability of component below a certain allowable level in regard to fast and time-dependent fracture. This is attained by satisfying design formulae written in the guide which limit the maximum stresses of specific section of the component to allowable values. The allowable stress values are given by the combination of the material strength, three design factors, and two safety factors. It should be noted that the proposed design guide is given only tentatively and should be refined and extended through experience.

1. Introduction

When using fine ceramics, which are new materials, as structural components, there must be design standards. This article puts forward a tentative plan on strength design standards for structural fine ceramic components.

Fine ceramics, which is essentially a brittle material, involve strength dispersion. To assure the safety of components using such material, it is deemed appropriate to hold the allowable fracture probability of the component within certain limits by a statistical method, taking the dispersion of strength of the material into consideration. In this design standards draft, however, the safety of components is evaluated by setting and using stress limitation tantamount to satisfying the allowable fracture probability.

2. Design Standards Draft for Preventing Instantaneous Fracture

The stress limitation expression given for preventing instantaneous fracture is

$$\sigma_s < \frac{1}{K_0 K_1 \beta_\gamma} \frac{S_u}{\gamma} \quad (1)$$

This expression can be obtained by computing the fracture probability of the entire component on the assumption that many cracks are distributed in the ceramic and that the fracture of each crack is governed by equivalent normal force Z

$$Z = \sqrt{\sigma_k^2 + (k\tau)^2} \quad (2)$$

The distribution of cracks is set so that the strength distribution of the ceramic under uniaxial stress may agree with the two-modulus Weibull distribution. In expression (2), σ_k is stress vertical to the crack face, τ is the shearing stress working on the crack face and

$$k = 0.5$$

is given for k , the constant, from the results of a breakdown test under multiaxial stress. The computation of fracture probability using expression (2) is rather difficult, and doing so at the time of designing is not considered appropriate. It would probably be better to make such computation in advance, consolidate the results in the form of expression (1), and give the coefficients contained in this expression in tabular form.

σ_k in expression (1) is nominal stress for the amount of load. In this standards draft, maximum stress in the part evaluated is used. The Prager-Drucker-Griffith equivalent stress is used in consideration of the state of multiaxial stress. When using some other nominal stress, it is necessary to change the value of β in Table 2. S_u is design minimum strength and computed as

$$S_u = \frac{S}{a} \quad (3)$$

by S , average tensile strength of the material, and a , design coefficient, in Figure 1. In Figure 1, m is the Weibull coefficient of the time when strength data are applied to two-modulus Weibull distribution. S , average tensile strength of the material, can be derived from its average bending strength using the concept of effective volume.

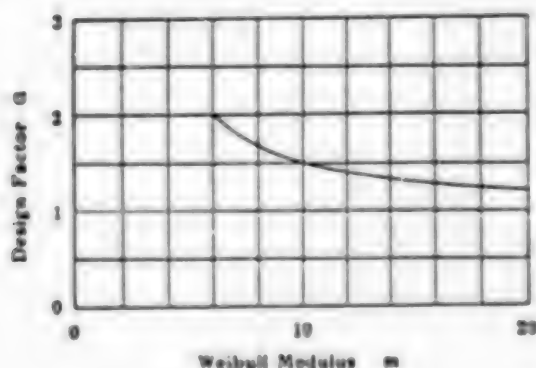


Figure 1. Values of Design Factor a


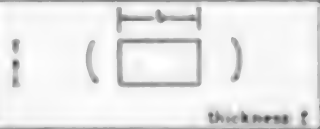

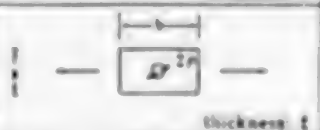

Table 1. Values of the Safety Factor K_1

| Class of components \ Loading conditions | Level A & B loading | Level C loading |
|--|---------------------|-----------------|
| Class 1 | 3 | 2.2 |
| Class 2 | 2.5 | 1.8 |
| Class 3 | 2 | 1.4 |
| Class 4 | 1.5 | 1.1 |

Safety factor K_1 is given, as shown in Table 1, for the combination of the relative importance of an apparatus and its state of operation. In this design standard, the relative importance of an apparatus is divided into four stages based on the extent to which its destruction affects other components, while its state of operation is divided into three states in consideration of the frequency of load exerted.

β , the design factor concerning stress gradient in the part in which stress is concentrated, and γ , the design factor concerning the spread of the part with high stress, are computed on the basis of the Weibull probability theory and are given as indicated in Table 2.

Table 2. Design Factors β and γ

| The shape of the local component and the loading pattern | | β | γ | Remarks |
|---|---|--|---|--|
|  thickness: t | | 1 | $\left(\frac{abt}{120}\right)^{\frac{1}{m}}$ | |
|  thickness: t | | $\left(\frac{1}{m+1}\right)^{\frac{1}{m}}$ | $\left(\frac{abt}{240}\right)^{\frac{1}{m}}$ | |
|  thickness: t | A | $\left(\frac{1}{m+1}\right)^{\frac{1}{m}}$ | $\left(\frac{abt}{120}\right)^{\frac{1}{m}}$ | When the neutral axis is within the cross section, select A, otherwise select A or B which gives smaller value of β . x : The distance between the maximum stress point and the neutral axis. |
| | B | 1 | $\left(\frac{abt}{120}\right)^{\frac{1}{m}}$ | |
|  thickness: t | | $-0.000171m^2$ $+0.0131m+0.071$ | $\left(\frac{abt}{120}\right)^{\frac{1}{m}}$ | |
|  thickness: t | | $\frac{1}{\sqrt{2}} \left \frac{1}{2(m+1)} + \frac{1-(1-C)^m}{2C(m+1)} \right $ | $\left(\frac{2\pi r^2 t}{120}\right)^{\frac{1}{m}}$ | $C = \frac{1+3\nu}{3+\nu}$ ν : Poisson's Ratio ω : Angular Velocity |

↓
Continue

Basic safety factor $K_0 = 1.3$ (provisional) is set with the object of absorbing on the safe side the difference between the Weibull distribution on which these computations are based and the reality, errors in stress computation, etc.

3. Design Standards Draft Aimed at Preventing Time-Dependent Fracture

As forms of ceramic fracture, there is not only instantaneous fracture but also time-dependent fracture for such reasons as static and dynamic fatigue. It is assumed that such time-dependent fracture is caused by slow crack growth and that the speed of the cracking progress can be expressed by

$$\frac{da}{dt} = AK^n \quad (4)$$

Here, a : crack length; t : time; K : stress expansion coefficient; and A, n : material constants. As an expression of stress limitation for such fracture,

$$\sigma_s < \frac{1}{K_0 K_1 \beta_\gamma} S_t \quad (5)$$

is given. This expression is identical to expression (1) except for the fact that S_t replaces S_u . S_t is the design minimum time strength, and can be obtained from the design fatigue curve and design time. Figure 2 provides a schematic diagram of the design fatigue curve. Three types of design fatigue curve--one for evaluating static fatigue, one for evaluating dynamic fatigue (partial swing), and one for evaluating dynamic fatigue (full swings) are made available in consideration of the effect of repetition on fatigue life.

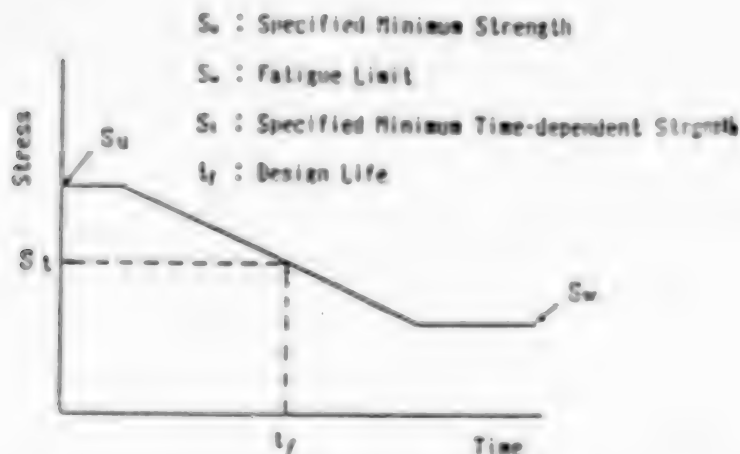


Figure 2. Schematic Diagram of Design Fatigue Curve

Strength of Ceramics Under Combined Stress

43063804g Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 187-189

[Article by Minoru Matsui, NGK Insulators, Ltd.]

[Text] **Abstract:** For using structural ceramic components under conditions of complicated stress, it is necessary to assure the reliability of the components. In order to investigate the fracture strength of ceramics under multiaxial loading, combined tension/torsion tests for sintered silicon nitride specimens have been carried out at room temperature. Tension, torsion, and four-point bending tests data were used for estimating Weibull's two parameters. The maximum tensile principal stresses at fracture for combined tension/torsion tests were higher with increased ratios $\tau(\text{torsion})/\sigma(\text{tension})$. The fracture stresses predicted by the Weibull statistical theory of uniaxial fracture and the statistical theory of multiaxial fracture for shear-insensitive cracks were in agreement with the experimental data. The fracture stresses predicted by the statistical theory of multiaxial fracture for shear-sensitive cracks were lower than the experimental data. Therefore, the statistical theory of multiaxial fracture which assumes a little contribution of shear stress to fracture can be used for designing components made of sintered silicon nitride.

1. Introduction

The state of stress of structural components in use environments is not uniaxial, but biaxial or triaxial. To use ceramics as structural components, therefore, it is necessary to accumulate data on the fracture strength of ceramics under multiaxial stress and to clarify their fracture patterns. In this research, fracture tests were conducted under combined tension/torsion stress using round bar test pieces of atmospherically sintered silicon nitride, and the strength data obtained were compared with predicted values by means of various fracture criteria.

2. Test Method

Buttonhead tension and torsion specimens measuring 6 mm in test section shell diameter and 24 mm in parallel section length were made of

atmospherically sintered silicon nitride with a density of 3.2 g/cm^3 . The shapes of the specimens are shown in Figure 1. Each torsion specimen was provided at either end measuring 12 mm each in width because it was to be charged with a torsion load. The parallel section of each specimen was finished using a #600 diamond grindstone. A crosshead speed of 0.05 mm/min and a torque speed of 0.005 kg-m/s were used for the tension test and the torsion test, respectively. For combined tension/torsion and compression/torsion stress tests, the torsion specimen shown in Figure 1(b) was used; τ/σ , ratio between τ , shearing stress by torsion, and σ , tensile stress, was varied; and tests were conducted under five conditions: $\tau/\sigma = 0.5, 1$, and 2 for the tension/torsion combination and $\tau/\sigma = -2$ and -1 for the compression/torsion combination.

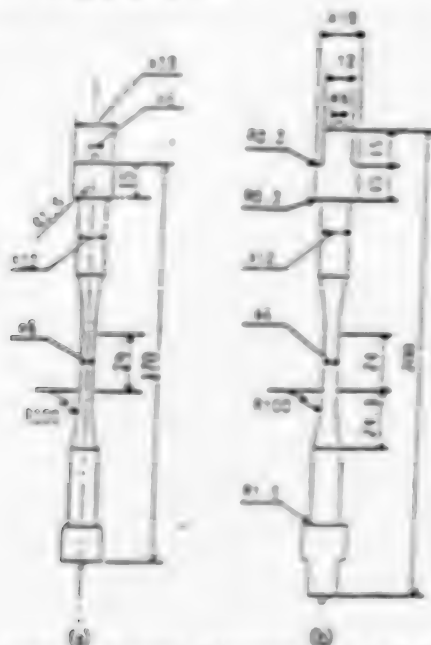


Figure 1. Geometry and Dimensions of Specimen
(a) Tension
(b) Torsion, combined tension/torsion

3. Test Results and Discussion

Figure 2 shows the Weibull plots of the tension, torsion, and four-point bending tests. The average strengths were, respectively, 524, 607, and 743 MPa, and they increased with the decrease of effective volume. Weibull coefficient $m = 15$ was obtained when the relationship between specimen average strength and effective volume was consolidated using Weibull statistics. This agreed well with the Weibull coefficient for the four-point bending strength with the largest number of specimens.

In tension/torsion, torsion and compression/torsion tests, θ , direction of maximum principal stress, can be expressed by $\theta = (1/2)\tan^{-1}(2\tau/\sigma)$ (Figure 3). The values of θ obtained by this expression were 23, 32, 38, 45, 52, and 58 for the stress ratios in the combined stress tests, $\tau/\sigma = 0.5, 1, 2, 0, -2$, and -1 , and agreed well with the directions of fractures where there were fracture starting points.

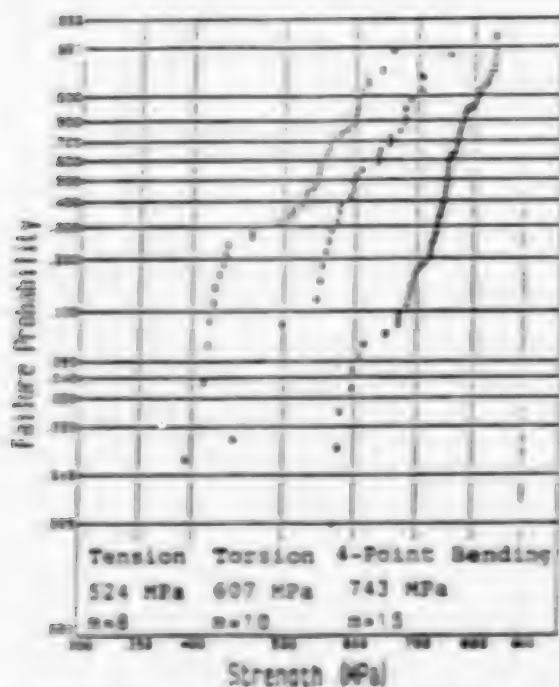


Figure 2. Weibull Plots of Tension, Torsion, and Four-Point Bending Strength

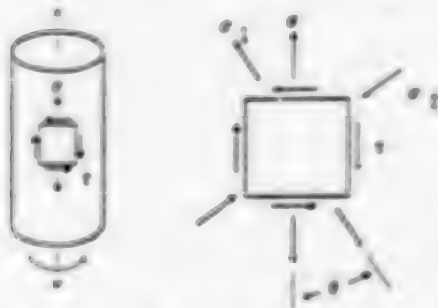


Figure 3. Stress State in Combined Tension/Torsion Loading

The results of the combined stress tests were consolidated by the ratio to the average tensile strength of principal stresses, σ_1 and σ_2 , obtained from the tensile stress and shearing stress due to torsion caused at the time of fracture (Figure 4). These data were compared with the predicted values by the uniaxial distribution function of strength and the multiaxial distribution using various fracture criteria. Namely, fracture strength was predicted by the following five strength distribution functions. This is shown with fracture curves in Figure 4.

- (1) Uniaxial distribution function (maximum principal stress theory)
- (2) Multiaxial distribution functions:
 - (a) Weibull's multiaxial theory (Weibull theory)
 - (b) G-criterion (co-planar crack extension)

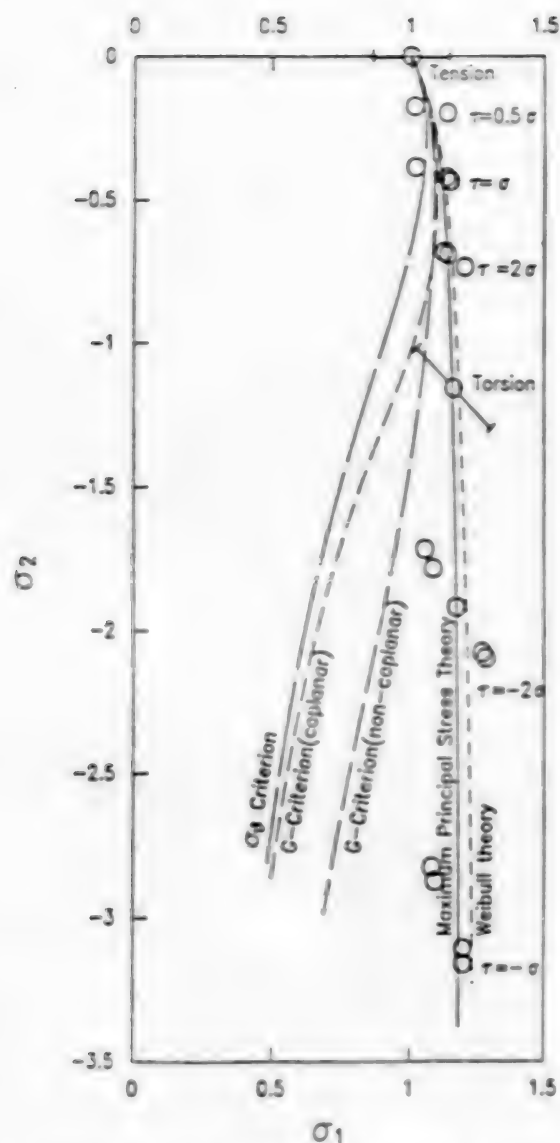


Figure 4. Experimental and Theoretical Fracture Stresses

(c) G-criterion (nonco-planar crack extension)

(d) σ_θ criterion

Of these, the maximum principal stress theory and Weibull's multiaxial theory do not take shearing stress into consideration, but the others take the contribution of shearing stress to fracture into account.

As indicated in Figure 4, the predicted value of the maximum principal stress was smaller than its test value when fracture criteria with consideration for shearing stress were used. Values predicted by the maximum principal stress theory and Weibull's multiaxial theory agree rather well with the test value. Therefore, either the maximum principal stress theory or Weibull's multiaxial theory can be used to evaluate fracture strength in the state of tension/torsion biaxial stress.

20108/9365

Development of Ceramic Hot Parts for Gas Turbine

43063804h Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 190-192

[Article by Yutaka Furuse, Engineering Research Center, Tokyo Electric Power Co., Ltd.: "Application of Ceramics to Electric Power Generating Gas Turbine"]

[Text] **Abstract:** Since 1984, Tokyo Electric Power Co., Ltd., has been conducting cooperation research program with Hitachi, Ltd., Toshiba Corp., and Mitsubishi Heavy Industries, Ltd., to develop ceramic hot parts for the next-generation power generating gas turbine.

The first goal of this program is the development of a 20 MW class gas turbine, and its turbine inlet temperature is set at 1,300°C to raise the efficiency of combined cycle power generation plant.

Following the fundamental research, the development program of combustor, nozzle, and bucket has been performed. The first step of this program will be completed successfully by the end of March.

1. Introduction

Since FY 1984, the Tokyo Electric Power Co., Ltd., has been conducting research and development on the application of ceramics to a gas turbine jointly with Hitachi, Ltd., Toshiba Corp., and Mitsubishi Heavy Industries, Ltd., with the object of developing a next-generation high-efficiency gas turbine (Table 1).^{1,2} The purpose of this R&D effort is to improve the efficiency of composite power generating equipment by using ceramics for hot parts, thereby making it possible to increase the temperature at the turbine inlet (to 1,300°C) and reducing the amount of cooling air necessary.

To make ceramic components practical, it is necessary not only to improve the characteristics of the material itself, but also to change the design concept drastically using a method that takes into account fully the characteristics of ceramics. In this development, we decided first to see the extent to which the design concept of a conventional metallic gas turbine should be changed in order to achieve a design making effective use of the merits of ceramics and overcoming their drawbacks.

Table 1. Master Schedule of Development

| | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 |
|--|----|--------|----|----|--------|----|----|--------------|----|----|----|
| Fundamental Research | | | | | | | | | | | |
| Application Research | | | | | | | | | | | |
| -Development of Component | | STEP 1 | | | | | | | | | |
| -Material Evaluation | | | | | STEP 2 | | | | | | |
| Combination Test of Small Scale Gas Turbine | | | | | | | | 20MW, 1300°C | | | |

Since FY 1985, we have been proceeding with development separately of the elements--combustor, stationary blade, and rotor blade--for a small 20 MW demonstration machine based on the results of the basic research conducted during FY 1984 and 1985, and we are scheduled to complete the first step of the development this fiscal year.

The following are some of our research results.

2. Results

First, we conducted basic research on evaluation of the characteristics of ceramics and assurance of their reliability. We are now making a comparative test of various materials and conducting research to establish a method to evaluate their reliability and other studies on the basis of the results of the basic research.

As elements in our research we are using metals for strong structural components and ceramics for heat resistant components to make effective use of the merits of ceramics.

For the combustor, which is exposed to hot combustion gas, we selected heat resistant atmospherically sintered SiC. As for its shape, we are studying two types: a ring type, easy to manufacture and assemble, and a tile type, advantageous for local thermal stress (Figure 1 [not reproduced]). In the atmospheric combustion test conducted at Step 1, we confirmed the soundness of both types.

For the stationary blade, we adopted a structure with separate blade and shroud so as to reduce thermal stress (Figure 2 [not reproduced]). For the two-stage stationary blade, we selected atmospherically sintered Si_3N_4 , but for the single-stage stationary blade, we are considering use of atmospherically sintered SiC because of its heat resistance. In the 3 ata medium-pressure test conducted in the current fiscal year, no abnormality was found to exist, but more severe thermal stress occurs at the time of emergency cutoff under actual pressure conditions. So we are studying ways to reduce the stress generated by means of shape and structural improvements.

In regard to the rotor blade, we are studying a structure to use a metal for the wheel, for which especially high reliability is required, and a ceramic (atmospherically sintered SiC) only for the blade, which is exposed to high temperature.

In this structure, great contact stress is caused by centrifugal force, and it is therefore important to develop a technique for joining ceramics and metals. We are now conducting studies to develop a ceramic insert material, as well as a metallic insert material for use between ceramics and metals (Figure 3 [not reproduced]). It has been confirmed that such material can withstand tensile stress corresponding to the centrifugal force in rated revolution. In regard to the rotor blade, there are conditions such as vibration as well as thermal stress and centrifugal stress, and it will take some time to develop. So we are also conducting studies on the development of a coating rotor blade using the flame coating of ZrO_2 .

Table 2. Operating Conditions of Ceramic Components (Approximate value)

| | Combustor | 1st stage | Nozzle 2d stage | Bucket |
|-------------------------------------|-----------|-----------|--------------------|--------|
| Gas temperature ($^{\circ}C$) | | | | |
| Maximum | 1,500 | 1,400 | 1,100 | 1,220 |
| Mean | -- | 1,300 | 1,000 | 1,150 |
| Gas pressure (ata) | 15 | 15 | 6 | 10 |
| Gas velocity (m/sec) | > 50 | > 700 | > 600 | > 600 |
| Promising material | SiC | SiC | Si_3N_4 | SiC |
| Surface temperature ($^{\circ}C$) | 1,300 | 1,380 | 1,080 | 1,200 |
| Thermal stress (MPa) | 60 | 340 | 140 | 400 |
| Centrifugal stress (MPa) | -- | -- | -- | 80 |

Table 2 shows the main conditions of use of ceramics by separate elements. Regarding strength, thermal stress in regard to the emergency cutoff of stationary and rotor blades is known to be extremely severe, but it is necessary also to take fully into consideration such factors as vibration and collision with flying objects. Also, durability against oxidation and corrosion by combustion gas of high temperature, high pressure, and high speed is a requirement.

3. Future Problems

Step 1 research in element technology development will be completed in the current fiscal year, and Step 2 research is to be started in the next fiscal year. Element tests for the combustor, the stationary blade and the

rotor blade will be conducted under conditions of actual pressure and actual temperature, and after the soundness of such element is confirmed, we will move on to assembly test research.

Very high reliability is required of power generating components. It is therefore necessary to increase reliability not only by reducing the load on ceramics by element and system research, but also by conducting research by which to grasp the long-term behavior of materials under actual use environments and thus make accurate life prediction possible.

Through the research conducted to date, development through improvement of existing materials as well as design improvements are in prospect, but to enhance reliability further, materials must have increased strength and toughness. In these circumstances, much is expected of the future development of new materials such as high-tenacity composite materials, for instance.

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20108/9365

Advanced Alloys With Controlled Crystalline Structures

43063804i Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 193-195

[Article by Michio Yamazaki, National Research Institute for Metals: "Outline of 'Advanced Alloys With Controlled Crystalline Structures'-- Nickel-Base Alloys and Ti Alloys"]

[Text] **Abstract:** "Advanced alloys with controlled crystalline structures" is the official name of a national project for alloy development sponsored by the AIST of MITI. Its basic idea is that one must control in a very sophisticated fashion alloy microstructures as well as alloy compositions. Four types of alloys are selected on these lines. They are single-crystal nickel-base superalloy, superplastic nickel-base superalloy, oxide dispersion strengthened nickel-base superalloy, and superplastic titanium alloy for high temperature use.

Three national research institutes and seven companies, as members of the "Research and Development Institute of Metals and Composite for Future Industries," are undertaking each role.

As an example from many noteworthy results, the developed oxide dispersion strengthened nickel base alloys, TMO-2, TMO-7 and others are the strongest superalloys in the world, though they are still experimental.

1. Introduction

"Advanced alloys with controlled crystalline structures" is not a general name but the name of a project based on the concept of improving characteristics by highly controlling the crystalline structures of alloys as well as their composition. This project is being executed by the Agency of Industrial Science and Technology as an 8-year plan for FY 1981 through FY 1988. In this session, the author outlines the project and then some of the organizations in charge explain their assignments; all of the organizations in charge will present their results in the poster session. Two special public lectures are scheduled on areas related to this project.

2. Research Setup

Commissioned to implement this project are three national research institutes as well as private firms, for which the commission was received by the Metal and Composite Material Research and Development Association, a foundation; seven companies that are supporting members of this association are handling research concerning alloys. (For short, these are referred to as A RI (National Research Institute for Metals), B RI (National Industrial Research Institute, Nagoya), C RI (Government Mechanical Engineering Laboratory), A Co. (Daido Steel Co.), B Co. (IHI), C Co. (Hitachi, Ltd.), D Co. (Hitachi Metals, Ltd.), E Co. (Kobe Steel, Ltd.), F Co. (Sumitomo Electric Industries), and G Co. (Mitsubishi Metal Corp.).)

3. Details and Technical Background of Research, and Outline of Principal Achievements

Four types of alloys--namely, three $\gamma + \gamma'$ Ni-base heat resistant alloys and an $\alpha + \beta$ Ti alloy were actually adopted as advanced alloys with controlled crystalline structures with a view primarily to use for gas turbines and jet engines.

3.1 Ni-base Monocrystal Alloy

This is Ni-base alloy that is made to be free of high temperature intercrystalline cracking during manufacturing or use. High temperature racks develop between columnar crystals from the core as a result of thermal stress during the cooling process after coagulation. Also, there are limits to the increase of strength because the rise in solution heat treatment temperature is limited by the carbon, etc., added to prevent high temperature cracking. Monocrystallization eliminates this drawback. A RI, which is in charge of alloy design, has proposed an alloy that exceeds the target. B RI, which is in charge of the core for manufacturing the hollow air-cooled turbine blade, has proposed a composition and process that can produce a core with high temperature strength and dimensional accuracy. A Co., which is in charge of research to manufacture an alloy material bar (melting stock) with a strictly controlled component percentage and almost without impurities, along with evaluation of its characteristics, has obtained satisfactory results. B Co. and C Co. are conducting research to manufacture hollow air-cooled monocrystal blades. D Co. and C Co. together are conducting tests to evaluate the monocrystal material. A skull melting formula using a plasma beam has been tested for monocrystal furnace melting to prevent impurities from infiltrating when the melting stock is remelted. The use of a resistance furnace to heat casting molds has been tested to suppress convection when monocrystals are growing. Also, the addition of a magnetic field for the same purpose has been tested. Contrivances used to increase temperature gradients in the vicinity of the part where coagulation is in progress include attachment of a booster heater and attachment of a shutter at the bottom of the casting mold.

The temperature distribution of the goods is assumed by means of computer simulation, taking heat conduction and radiation into consideration, and is used for reference in controlling lowering speed, etc.

The prospects are that by means of this research, complex-shaped product using the alloy developed will be obtained.

3.2 Ni-Base Superplastic Alloy

Cracks develop as a result of ordinary melting plus forging when the amount of γ' in the Ni-base alloy is increased to improve the strength of turbine disks for jet engines, etc. So the method of powder metallurgy is used, but it is believed that only low reliability can be achieved by just caking powder by means of HIP. Therefore, a study is being made of a process to prepare a preform from powder and make it into a product by means of superplastic forging. The incorporation of high temperature extrusion in preform manufacture is ideal because it facilitates crystal grain refining, but a large extruding machine is necessary to produce large components, so it is uneconomical. In this project, therefore, we are studying how to make preforms by HIP only and work them superplastically. The same applies to the Ti alloy to be described later.

A RI, which handles alloy designing, has obtained alloys with satisfactory superplastics characteristics, but the strength characteristics are only slightly better than the world level and have not attained their targets yet.

C RI, which is in charge of basic research on superplasticity manifesting mechanisms, is placing special emphasis on the study of forging molds. Also, it is attempting to achieve considerably faster forging than is accomplished in ordinary superplastic forging by mantling preforms with carbon steel sheaths to lower mold temperatures and using molds heated to about 600°C.

To produce fine powder, we use centrifugal atomization (quenched by liquid helium in this process; A Co.) and argon gas atomization (E Co.), causing the melt to fall onto a rotary disk. In centrifugal atomization, the disk must be turned rather rapidly to obtain fine powder.

E Co. research on forging concerns a 400 ϕ bossed disk and a disk (150 ϕ) with complex blades. The former is also used for research on how to process a dual property disk wherein the composition differs between the periphery of the disk and its interior. Computation by finite element method is also being attempted in order to determine the shape of a preform wherein the degree of processing is uniform in different parts of the disk.

F Co. is seeking to improve superplastic characteristics by stressing through the (attriter) treatment of powder. One problem with this is the infiltration of impurities by the (attriter).

C Co. is studying how to use the superplasticity of thin-film material for the joining purpose. To produce thin film, the melt is quenched by the double roller method. The company is considering use of this method for the joining of particle dispersion reinforced alloy.

3.3 Ni-Base Particle Dispersion Reinforced Alloy

Research is underway on how to process by (attriter) the elemental powder, alloy powder and yttria powder of an alloy of the composition designed by A RI, extrude them (F Co.), make the extruded bar into the approximate shape of the product by isothermal forging (E Co.), and produce it as a component by joining after band annealing and unidirectional recrystallization (B Co.). A TMO-2 alloy far exceeding the target strength in the state without intermediate forging has been proposed, and research is being conducted on how to manufacture and process it. In particle dispersion reinforcing, which does not involve grain boundary reinforcing, it is essential to elongate the crystal grains greatly by unidirectional recrystallization. This is technically a rather intricate treatment, especially because unidirectional recrystallizing is difficult if the extruded material is subjected to isothermal forging before band annealing. TMO-7, stronger than TMO-2, has also been developed.

3.4 Superplastic Ti Alloy

A Ti alloy with high specific strength (300°C) capable of being superplastically forged into complex shapes is being developed with a view primarily to use for gas turbine compressor disks. A RI has devised a design method resembling the design of Ni-base alloy, and it has developed some $\alpha + \beta$ alloys that have strength characteristics better than their targets and can be processed superplastically. It has also devised an empirical formula that it is using to estimate the strength and superplastic characteristics from the composition and quantities of α and β phases. GT-33 alloy is proposed as a candidate alloy.

G Co. is in charge of research on powder manufacture and superplastic forging. In the case of Ti alloy preforms for superplastic forging can be made without recourse to powder metallurgy, but in order to minimize the segregation of large members, the use of powder metallurgy method is preferable. The company is studying how to manufacture 400 ϕ bossed disks using the PREP (plasma beam rotary electrode process) to manufacture powder.

20108/9365

Superplastic Forging of Nickel-Based Superalloy Disks

43063804] Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 198-200

[Article by Osamu Tsuda, Dr Tomiharu Matsushita, Dr Kenji Iwai, and Selya Furuta, Research and Development Division, Kobe Steel, Ltd.]

[Text] **Abstract:** A new superplastic forging process for nickel-based superalloys has been developed, in which very fine gas atomized powder is consolidated to billets through the HIP process and forged directly under isothermal conditions.

Prior to actual forging, numerical simulations were conducted by using rigid plastic FEM to find out optimum forging conditions. It is shown that the height-to-diameter ratio of the billet is one of the most important parameters in regard to strain distribution. The calculated forging loads show good agreement with experimental ones.

Superplastic forging equipment for producing gas turbine disks with 400 mm diameter was designed and built. The HIP billets from modified IN100 superalloy powder were successfully forged into disks with boss with the maximum forging load of 1,500 tf in superplastic condition.

The mechanical properties of the disk were examined. The results show that the structures of the forged products are homogeneous particularly in the area applied to large strain, and that they have as good tensile properties as those from the gatorizing process and much more excellent low-cycle fatigue property than as HIP products.

1. Development of HIP Material for Superplastic Forging Using Very Fine Powder Produced by Ar Gas Atomization

The technology of manufacturing a material with very fine crystal grains so as to cause superplasticity is important to the superplastic forging of Ni-base superalloy to be used as the material for the high-temperature gas turbine disks for jet engines and generators. Conventionally, the method known as gatorizing process¹ to obtain a fine crystal texture through recrystallization by hot extrusion this super process has been used for crystal grain refining. Now, the authors have not only newly developed

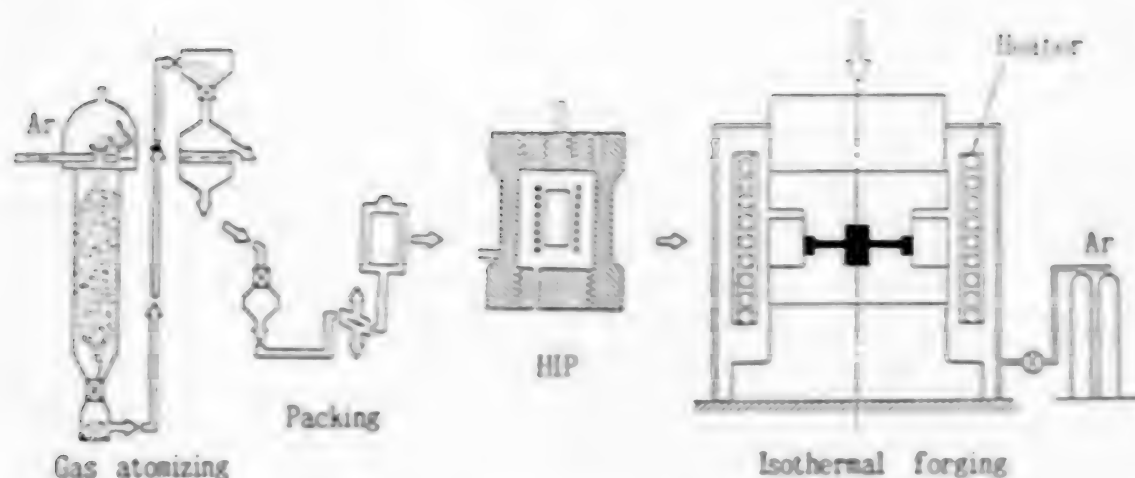


Figure 1. New Superplastic Forging Process

fine powder manufacturing by Ar gas atomization, as shown in Figure 1, but also they have ascertained the superplastic behaviors appear when fine superalloy powder is HIP-treated, and thus they have established the technology of manufacturing a material for superplastic forging.

2. Simulation of Deformation in Superplastic Forging

Forging simulation² was accomplished using a rigid plastic finite element method to analyze material deformation in superplastic forging and to determine optimum forging conditions. This analytic program is characterized by the fact that it can deal with strain hardening and rate of strain dependency; that metal mold boundaries can be divided into straight lines, parabolics, arcs, etc.; and that velocity and frictional condition can be defined separately by component. Furthermore, it made possible the redivision of elements that is necessary to handle the major deformation.

Figure 2 shows the $pst-f$ equivalent strain distribution analyzed by this forging simulator for two types of material shapes. In the analysis, 0.5 was used as m -value, the rate of strain dependency index of the material, and 0.3 was used as the coefficient of shear friction between the metal mold and the material. In Figure 2(a), height/diameter $H/D = 0.56$ of the forge material. The equivalent strain is rather large in the periphery of the disk and it is maximum (about 2.5) on the outside of the boss. The part under the boss is hardly deformed. In Figure 2(b), $H/D = 0.16$. The strain distribution is rather uniform in the part under the boss and it is maximum (about 1.6) on the inside of the boss, but in a periphery corner of the disk, there is an undeformed area. The optimum shape of forged material from the viewpoint of equivalent strain distribution is achieved when strain distribution is uniform as a whole, and that is believed to be intermediate between these two.

An analysis of the state of material filling the metal mold revealed that a perfect fill is easy to attain and the forging load is small with the

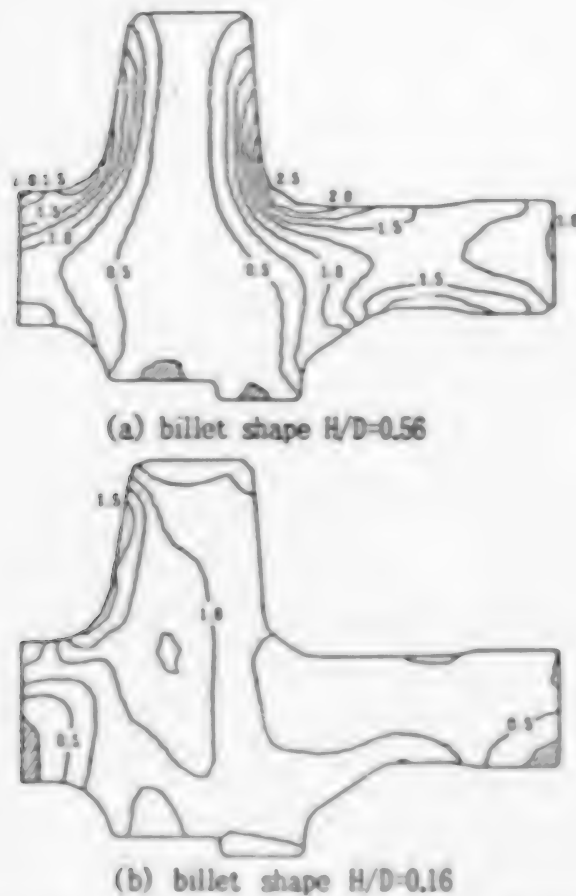


Figure 2. Equivalent Strain Distribution by Rigid Plastic FEM Analysis

material shape $H/D = 1.77$, at which filling is completed almost simultaneously in the boss part and the periphery. The relationship between stroke and forging load determined by the analysis agreed well with the load data in forging a disk with a reduced-size boss measuring $\phi 150$ mm in outer diameter and a disk with a $\phi 400$ mm boss.

3. Superplastic Forging of Bossed Disks

A 400 tf superplastic forging press composed of a chamber device, a heating coil, a manipulator, etc., was designed and manufactured for the research and development of superplastic forging technology; the technology of molding superalloy turbine disks was basically established by superplastically forging disks with reduced-size bosses measuring $\phi 150$ mm in outer diameter using this press.³ Based on this achievement, a large forging system was manufactured to forge-mold disks with bosses measuring $\phi 400$ mm in outer diameter. The chamber device is composed of top and bottom cooling panels, sidewalls and controls using Ar gas atmosphere. The heating coil, which is a low-frequency induction coil of 60 Hz x 550 kW, can simultaneously heat the metal mold and the forge material. It also measures temperature, pressure, oxygen concentration, etc., and controls press speed, Ar gas flow rate, heating coil position, etc. The forging die is composed of a TZM metal mold, a knockout rod, an insulated runner mold and a supporting metal mold. The thicknesses of the TZM metal mold and the

insulated runner mold were decided by heat transfer analysis. The ram speed in superplastic forging can be preset-controlled within the range of 0.1 - 300 mm/min.

The forge material was prepared using HIP caking powder of Ni-base superalloy Mod IN100 (0.07C-12.4Cr-18.5Co-3.2Mo-4.3Al-5.0Ti-0.8V-0.020B-0.06Zr-bal Ni) with a grain size of 105 μm having undergone Ar gas atomization. Forging was performed at a temperature of 1,050°C and an average rate of strain of $2 \times 10^{-4} \text{ sec}^{-1}$.

Figure 3 compares the relationship between the stroke and forging load measured at the time with the results of analysis. It indicates that the forging load was only about 200 tf at the beginning and middle part of forging, but that it rapidly increased as the material was loaded and finally reached 1,500 tf.

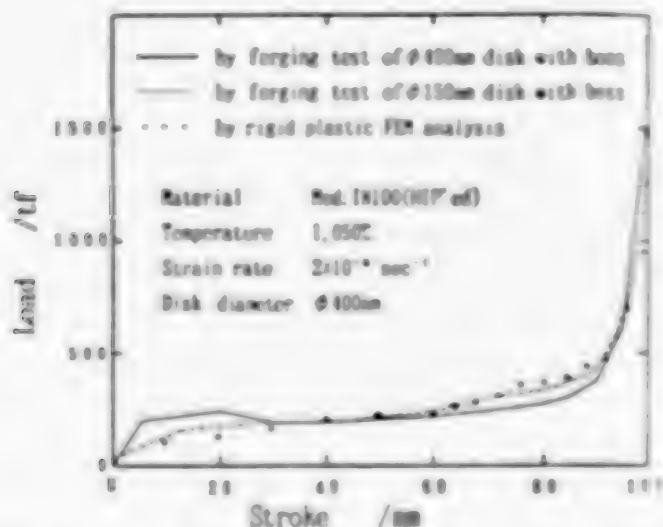


Figure 3. Forging Load for Superalloy Disks With Boss in Superplastic Condition

4. Material Strength Characteristic of Disks With Large-Diameter Bosses

After forging, the material, as is, was checked for material strength characteristics by subjecting it to four-stage heat treatment (1,175°C x 3 h/FC + 1,080°C x 4 h/AC + 843°C x 16 h/AC + 760°C x 24 h/AC). The crystal grain size after heat treatment was 15 μm because the coarsening of the crystal grains had been suppressed by using a low heat treating temperature. So the rupture life in the stress rupture test (testing temperature 760°C x load stress 60.5 kgf/mm²) was shorter than that of as-HIP material with a grain size of 40 μm , but strength and ductility in the tension test (four stages from room temperature to 760°C equaled those of small specimens of the same material having received heat treatment. Thus, the material strength characteristics are indeed excellent. In a low-cycle fatigue test performed at testing temperature 635°C x repetitive load stress of 0.112 kgf/mm², the number of repetitions until rupture was more

than 10^6 ; thus, the characteristic was excellent. This value means a life about 10 times longer than the actual value of as-HIP material.*

This research was conducted as part of the "research and development of advanced alloys with controlled crystalline structures" under the Next-Generation Industrial Basic Technology Research and Development System

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20108/9365

Superplastically Forged Titanium Alloy Powder Preforms

43063804k Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 201-203

[Article by Toshio Kimura, Central Research Institute, Mitsubishi Metal Corp.]

[Text] **Abstract:** Titanium alloys GT-9 and -33 were designed by NRI to have good superplasticity at working temperature and superior mechanical properties at service temperature. We examined the processing characteristics, the mechanical properties, and the superplastic behavior of P/M titanium GT-9 and -33 alloys.

Titanium alloy powder with a mean particle diameter of 70 to 200 μm was obtained by the plasma beam rotary electrode process and consolidated by hot isostatic pressing.

HIP preforms were forged superplastically to the miniature disk at very low forging pressure.

The forged and heat-treated GT-33 alloy showed good combination of UTS 130 kgf/mm² and elongation 12 percent at 300°C.

1. Introduction

Titanium alloys are excellent as materials for aircraft and gas turbines because of their characteristically high specific strength. But based on the science of alloys, it appears that there is room for characteristic improvement. Also, the present procedure for manufacturing them is under processing restrictions so great that the yield is extremely low. Therefore, the "superplastic alloy technology" in the advanced alloys with controlled crystalline structures project is aimed at developing alloys having high strength and high ductility at service temperature and high superplasticity at working temperature and at developing a working process for this purpose. In the working process, fine powder is used as the starting material, and taking advantage of the high superplasticity caused by its subsystem, superplastic forging is performed at a low load and superplasticity is obtained by post heat treatment. The target of development are: 1) specific strength of at least 28 kgf/mm²/g/cm³ at

300°C; 2) elongation of at least 10 percent at this time; and 3) working yield achieved by means of superplasticity at least three times the level achieved by the conventional method. The National Research Institute for Metal is in charge of alloy development, and we are in charge of developing the working process. This report outlines the results of the period up to the current fiscal year.

2. Alloys Developed

As will be reported separately, the National Research Institute for Metals developed GT-9 as a "jisedai" (next-generation) alloy and then GT-33 meeting performance targets, by a newly developed alloy designing method. Their composition is shown in Table 1. Both are $\alpha + \beta$ two-phase alloys. We developed a manufacturing process for each and made characteristic evaluation tests using the two alloys and Ti-6Al-4V.

Table 1. Alloy Development Constituent Specification Values

| | Al % | V % | Sn % | Zn % | Mo % | Cu % | Fe % | O % |
|------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|----------|
| GT9 | ± 0.3 5.6 | ± 0.2 0.5 | ± 0.2 1.2 | ± 0.2 3.6 | ± 0.2 0.9 | ± 0.2 1.2 | ± 0.2 0.9 | 0.1.~0.2 |
| GT33 | ± 0.3 6.5 | ± 0.2 1.3 | ± 0.2 1.0 | ± 0.2 1.0 | ± 0.2 2.6 | ± 0.2 2.1 | ± 0.2 1.6 | 0.1.~0.2 |

3. Powder Manufacture

To manufacture Ti alloy powder, the main method is the centrifugal atomizing method, consisting of melting the rotating electrode end face and atomizing by centrifugal force. But we developed a rotary electrode method using a plasma beam for heat as a process with only small constituent variation and only small oxygen pickup. The powder grain size is determined by the circumferential speed of the electrode, and powders with an average grain size ranging from 70 to 200 μm were produced (Figure 1 [not reproduced]).

Concentrated Zr layers with a surface layer of about 200 Å were observed in some of the GT-9 alloy powder obtained, but no constituent variation including oxygen could be seen.

A cooling gas jet nozzle is provided in the powder flying path of this device. As the substructure of the powder, cells of 2 to 6 μm are present. It is assumed from the empirical formula obtained for other alloy systems that the cooling velocity of Ti alloy powder is 10^2 ~ 10^3 K/sec.

4. HIP

HIP was used to mold alloy powder into billets for forging, and the effects of HIP conditions on the structure were investigated. At low temperature, α shells remain in PPB. In the $\alpha + \beta$ two-phase zone, the crystal grain size of HIP material is proportional to the first or second power of

pressure and to time and in reverse proportion to the inverse degree of temperature. A check on superplasticity revealed that the n -value was about 0.4 in the HIP state, and the total elongation was only about 270 percent.

5. Superplastic Forging

We designed and manufactured a 200-ton superplastic forging press for test use, performed an upsetting test on HIP material and checked on its superplasticity. HIP material has only small resistance to deformation because of its minute structure, and it becomes a fine equi-axed structure as the effect of PPB disappears with a relatively small strain. Also, crystal grain size during superplastic forging can be readjusted by Zener parameter A . Taking advantage of this, we were able to improve superplasticity by refining the crystal grains in the course of forging. Forgings have equi-axed crystals of about $2\text{ }\mu\text{m}$, eventually exceed 0.85 in n -value and 1,000 percent in total elongation, and their deformation resistance greatly decreases in the low rate-of-strain zone. Taking advantage of this, we superplastically forged models of disks with $\phi 150\text{ mm}$ blades (Figure 2 [not reproduced]).

When extruding to the blade section, mold filling performance was most satisfactory as a result of the improvement of the material fluidity attending superplasticity. With these results in view, we accomplished $\phi 400\text{ mm}$ life-size disk forging using a 4,000-ton press. Drastic reduction of forging force, improvement of material fluidity and improvement of mechanical properties through the homogenizing of the structure were achieved by using superplasticity for forging.

6. Evaluation of Characteristics

Strength and elongation were measured after the solution treatment and age treatment of superplastically forged pancake material. At 300°C , the specific strength of GT-9 alloy was $29.4\text{ kg/mm}^2/\text{g/cm}^3$ and the elongation was 6 percent. With GT-33, the targets were attained as its specific strength and elongation were, respectively, 28.7 (UTS 131.8 kgf/mm^2) and 11.6 percent. We also evaluated fatigue and creep characteristics. Characteristic evaluation was also made of disk forgings.

7. Summary

We developed the process of powder manufacture-HIP-superplastic forging using "jisedai" developed alloys, and achieved our targets. The remaining year of our research period will be used to analyze and improve the various processes and tentatively to manufacture life-size disks with blades. We also intend to improve the various characteristics in actual disks.

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Study of Die, Lubricants for Isothermal Forging

430638041 Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 204-206

[Article by Yoshinori Nakazawa, Mechanical Engineering Laboratory]

[Text] **Abstract:** In order to clarify the effective combinations of the die materials and the lubricants in isothermal forging of titanium alloy Ti-6Al-4V and nickel-base alloy Mod IN-100, isothermal ring compression tests are performed in a vacuum to prevent oxidation of materials. The forging temperature is 900°C for the titanium alloy and 1,050°C for the nickel-base alloy. The die materials used are four refractory metals, TZM, TZC, MHC, and W2ThO₂; two nickel-base cast alloys, IN-100 and TRW-NASA-VIA; and two ceramics, SiC and BN. The lubricants used are glass, graphite, and BN powders suspended in water, isopropanol or xylene. After forging height and inner diameter of the ring specimens are measured, and the frictional shear factor for each case is obtained by using the calibration curves calculated by Lahoti, et al. As to results, the combination of glass in water and refractory metal die gave the lowest frictional shear factors: 0.1 for titanium alloy and 0.13 for nickel-base alloy. SiC die with glass lubricant gave a slightly higher frictional value: 0.2 for titanium alloy and 0.25 for nickel-base alloy. In both cases, sound products could be obtained. On the other hand, small chipping on the surface of the ceramics die occurred.

1. Introduction

The use of isothermal forging wherein the forging die is heated to the temperature of the work material and maintained at this temperature level is being considered as a method to mold hard-to-work materials such as titanium and nickel-base alloys. The working conditions when using, say, nickel-base superplastic alloy as the working material are a high temperature of more than 1,000°C and a low rate of strain of about 10^{-3}s^{-1} . This means very severe use environments for die materials, and furthermore, a diffused junction between the work material and the die material can easily occur in this situation. Thus, it is important to select a die material that can withstand such a high-temperature environment and to select or develop a lubricant that not only prevents a diffused junction but also reduces frictional force.

The authors have so far conducted research on the high-temperature characteristics of various materials believed to be usable as isothermal forging die materials and on the work and lubricant characteristics in the isothermal forging of titanium and nickel-base alloys using these die materials. This report describes the result of an isothermal forging test made on titanium alloy and nickel-base alloy using various die materials and lubricants and of a ring compression test made to ascertain how various combinations of work materials, die materials, and lubricants affect working characteristics and lubricant characteristics in isothermal forging.

2. Test Conditions

The titanium alloy used as Ti-6Al-4V fused material and the nickel-base alloy was Mod IN-100 obtained by means of powder metallurgy. From these materials, ring compression test pieces having a shape and size ratio of 6:3:2, namely 15 mm for outer diameter, 7.5 mm for inner diameter and 5 mm for height, were prepared by machining. The names and specifications of the lubricants used in the tests are shown in Table 1, while the names of die materials used in the tests are shown in Table 2. The dies used were cylinders measuring 30 mm in diameter and 22.5 mm in height.

Table 1. Lubricants Used

| Glass | | Graphite | | BN |
|--------------------------|-----------------------------|-----------------------|-----------------|----|
| 1 Deltaglaze 19 (w) | 5 Deltaglaze 37 (re+xy) | 8 Deltaforge 21 (w) | 12 TK 12497 (w) | |
| 2 Deltaglaze 69 (w) | 6 Deltaglaze 349 M (re+iso) | 9 Deltaforge 31 (w) | | |
| 3 TK-12759 (w) | 7 Deltaglaze 29 (w) | 10 Deltaforge 144 (w) | | |
| 4 Deltaglaze 347 M (iso) | | 11 Deltaforge 182 (w) | | |

(Carrier and binder) w: water, iso: isopropanol, xy: xylene, re: resin.

Table 2. Die Materials Used

| | | | | |
|-------------------|----------|----------------|-------|-----------------------|
| Refractory metals | a TZM | b TZC | c MHC | d W-2ThO ₂ |
| Super alloys | e IN-100 | f TRW-NASA VTA | | |
| Ceramics | g SiC | h BN | | |

The whole isothermal forging die composition shown in Figure 1 was set in the chamber of the testing device, and forging was performed at 1,050°C for nickel-base alloy and at 900°C for titanium alloy. A constant velocity of 0.01 mm·s⁻¹ was used for working so that the rate of strain at the initial period of upset might be 2 x 10⁻³s⁻¹, and the upset was continued until a draft of 50 percent was reached.

3. Test Results

The lubricant completely adhered to the surface of the test piece after upsetting by metal die, and no junction with the die occurred. But in the case of glass-based lubricants containing resins (items 5 and 6 in Table 1), the resins hardened in the process of cooling, making it

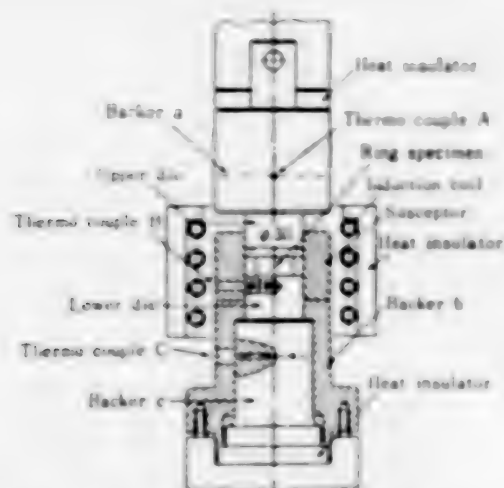


Figure 1. Schematic Diagram of Forging Apparatus
Backers and susceptor are made from molybdenum alloy TZM

difficult to detach the work material from the die, and the work material sometimes had to be removed by exerting slight impact force with a hammer or other tool. The primary purpose of use of the BN die was to ascertain whether forge molding without a lubricant was possible, taking advantage of the function of BN itself as a lubricant. But the work material became deformed as it cut into the die, the load suddenly increased at the start of deformation, and the die broke when 1,000 kgf was somewhat exceeded. Ring compression by SiC die can be performed satisfactorily and without die destruction if a glass-based lubricant is used for titanium alloy or nickel-base alloy, but the load value is 5 percent higher than with a high-melting-point metal die.

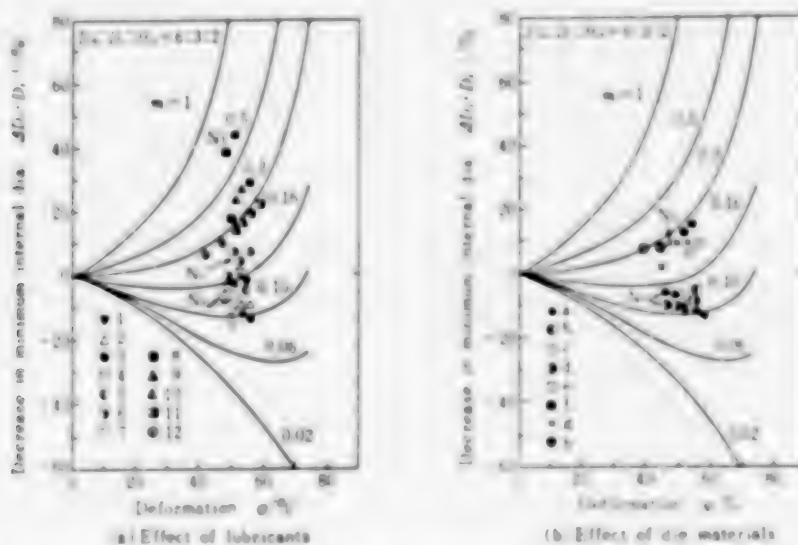


Figure 2. Frictional Shear Factors Obtained by Isothermal Ring Compression
Material marks shown by numbers or alphabets in figure correspond to those in Table 1, 2 and Ni mark points show Mod. IN-100 ring specimen and other no mark points show Ti-6Al-4V.

Figure 2 shows the values of shearing friction coefficients obtained from these tests. The symbols used correspond to the symbols for the various materials in Tables 1 and 2. When accompanied by the symbol Ni the work material is nickel-base alloy, and when no symbol appears the work material is titanium alloy. In Figure 2(a), TZM was used as the die material and various lubricants were used. In Figure 2(b), the lubricant was a glass type (TK-127 59), giving a low value of friction coefficient, and various die materials were used.

4. Conclusion

We conducted a ring compression test on titanium alloy and nickel-base alloy to see how the various combinations of lubricants and die materials affected working characteristics, etc., in isothermal forging. It revealed the following:

- (1) A satisfactory temperature distribution where temperature around the work material is nearly uniform can be obtained by arranging soaking rings around the die.
- (2) In the BN die, destruction or indentation in the ring shape of the work material occurs during compression, making its independent use difficult.
- (3) In the SiC die, pressurization without destruction, etc., is possible, but chipping develops if it is continuously used several times. If defects including small surface cracks can be suppressed to some extent, ceramics can be used in the atmosphere. Thus, it is considered hopeful as a simple-shaped die for isothermal forging.
- (4) If a glass-based lubricant and a nickel-base alloy die are used together, the lubricant adheres to the die.
- (5) The value of the shearing friction coefficient is lowest when a high-melting-point metal die and a glass-based lubricant with water as solvent are used. It is about 0.1 for titanium alloy and about 0.13 for nickel-base alloy.
- (6) The value of shearing friction coefficient in a ceramic die is higher than in a high-melting-point metal die. It is about 0.2 for titanium alloy and about 0.25 for nickel-base alloy.

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Strength, Plasticity of Intermetallic Compounds

43063804= Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 207-209

[Article by Masaharu Yamaguchi, Department of Metal Science and Technology, Kyoto University]

[Text] **Abstract:** In the past 10 years, many advances have been made in research on intermetallic compounds with potential applications for high-temperature structural materials. One of the highlights of these advances is the finding of the beneficial effects of boron on grain boundary ductility of Ni_3Al . It should also be noted that significant progress has been made in the improvement of ductility of NiAl and FeAl by control of the stoichiometry and by refining the microstructure. Another point of noteworthy progress is the development of TiAl -base alloys with some tensile ductilities at room temperature and a higher strength/density ratio than the conventional Ni-base superalloys. This paper is intended to demonstrate the state of our current knowledge of the mechanical properties of these aluminides.

1. Introduction

Technological innovation with a view to 21st-century industries is in progress in all branches of technology, including the information-related area. But to achieve innovation in the highly developed technology systems of today, the appearance of new materials to make this possible is essential. As far as metallic materials are concerned, such new materials no longer seem likely to be found from among the presently available metals and alloys, and endeavors are now underway to find them from among the group of new substances. The group of new substances include nonequilibrium alloys such as amorphous alloys and ODS alloys obtained by mechanical alloying. They are intermetallic compounds that have been all but ignored as detrimental and used only as dispersoids for the age hardening of alloys. This article deals with these intermetallic compounds, and, noting some that are anticipated as new structural materials, particularly materials for heat-resistant structures, explains their strength and plasticity. At the same time, we shall discuss problems that must be overcome to make these compounds practical.

2. Transition Metal Aluminides

Atoms composing an intermetallic compound are arranged with mutual regularity, their interatomic bonding is strong and their crystalline structure is often complex. So, on the whole, these compounds are brittle materials lacking in plasticity. From this standpoint alone, intermetallic compounds are indeed detrimental to structural materials. But their strong bond, which causes this brittleness, also causes hardness and strength--an advantage of intermetallic compounds. Also, in the case of high-melting-point intermetallic compounds with a large content of Al and other highly acid-proof elements, it enables these elements to be maintained stably up to high temperatures and to demonstrate their great resistance to acids. In these circumstances, intermetallic compounds as structural materials have been, and are still, used mainly as wear-resistant materials due to the advantage of their hardness and as heat resistant materials due to the advantage of their high-temperature strength and the acid-proof property of their component elements. It is no exaggeration to say that the question of how to assure minimum cold ductility or tenacity necessary for practical use while maintaining hardness and heat resistance has formed the history of developing practical structure-use intermetallic compounds or structural materials based on intermetallic compounds.

Chief among the intermetallic compounds that have hitherto been studied as heat resistant materials are transition metal aluminides because of the necessity for them to be highly acid-proof and have a high melting point--notably, Fe-group elements (Fe, Ni, Co) and Ti aluminides with simple crystal structures from which plasticity can be expected. We shall now look at the present studies on these aluminides and the problems that must be solved to make them practical.

2.1 Ni₃Al and Ni₃Al-Base Tertiary Compound

The present Ni-base superalloy is reinforced by Ni₃(Al, X) tertiary compound comprising Ti, Al, Nb, and Zr solid solutions on Ni₃Al. Since the volume ratio of the reinforced phase is now 60 percent, it would be more appropriately called Ni₃Al-based than Ni-based. In this sense, Ni₃Al and Ni₃Al-base tertiary compounds are the most important practical heat resistant intermetallic compounds of the present time. As is known, not only Ni₃Al but also other Ni-base L1₂ intermetallic compounds show a reverse temperature dependency of strength, which is due to the fact that cross-slip is caused by the anisotropy of energy on the antiphase boundary (APB) and dislocation becomes established. The greatest obstacle to the making of practical intermetallic compounds formerly was the low plasticity of polycrystalline materials due to a brittle crystal grain boundary, but now adequate plasticity can be given to polycrystalline materials by reinforcing the grain boundary through the addition of a small quantity of B. Furthermore, basic knowledge has been accumulated on the mechanism of boundary reinforcement by the addition of B, the step-up of solid solution of Ni₃Al, the creep mechanism and other matters. An Ni₃Al-base tertiary compound permitting deep-draw working and surpassing the conventional general Ni-base superalloys in specific strength has already been developed. However, it is heavier than the TiAl intermetallic compound to

be described later, and some think that it may be difficult to apply to future technologies such as those for new hypersonic aircraft of the future.

2.2 NiAl, FeAl, and Other Intermetallic Compounds With Regular bcc Structures

NiAl, FeAl, and CoAl are high-melting-point intermetallic compounds with simple B2 structure; their Al content, which is higher than that of Ni₃Al, makes them superior in resistance to oxidation, and their specific gravities are small. But they generally lack plasticity because they are basically of bcc structure, a structure wherein lattice friction against the movement of dislocation is great. It has recently become known, however, that pseudoductility reaching a few percent to scores of percent at more than 300°C for NiAl and at room temperature for FeAl can be obtained by refining the crystal grains. These new findings are noted as paving the way for improving the plasticity of this type of compound. In strength, NiAl, for instance, surpasses Ni₃Al and Ni-base superalloy at low temperatures, but at high temperatures, it is known to be inferior, particularly in creep strength. Therefore, to make such intermetallic compounds practical hereafter as structural heat resistant materials, it is necessary to improve not only their plasticity at low temperatures but also their creep strength at high temperatures. The strength and plasticity of several intermetallic compounds similar to the B2 type but with more complex structures are being investigated, but none with excellent creep strength and low-temperature plasticity have been found so far.

2.3 Ti-Al Intermetallic Compounds

In the Ti-Al group there are three types of intermetallic compounds: Ti₃Al, TiAl, and Al₃Ti. Of these, TiAl surpasses Ni-base superalloy in specific strength and it excels in resistance to oxidation, so it is considered as a new lightweight heat resistant material. TiAl turbocharger rotors are already in production and have proved to excel in rotation acceleration and other capacities because of their light weight. Based on constitutional diagrams, TiAl has a fairly broad compositional zone, but research on practical use is concentrated on materials with compositions near the phase boundary showing cold ductility of several percent (~ 36 wt% Al). TiAl has a tetragonal L1₀ structure based on an fcc lattice, and when it is deformed, a so-called ordered twin that does not disturb the regular arrangement of Ti and Al develops. It is this ordered twin that handles TiAl deformation. So, to improve cold ductility further it is necessary to devise a means to facilitate the generation and propagation of the ordered twin. If an alloying method is employed, efforts must be made to find an element conducive to lowering the stacking fault energy of TiAl. In a composition important from the practical point of view, meanwhile, it is necessary to clarify the relationship between the laminated structure of twin crystals and Ti₃Al already developed after coagulation and the deformation characteristic of TiAl. For wide use of TiAl in the future, control of this structure will be important. At high temperatures, the reverse temperature dependency of strength appears, as in the case of

Ni₃Al, but the mechanism at work in this connection has yet to be ascertained.

The TiAl intermetallic compounds include Al₃Ti, which contains even more Al than TiAl does. This compound surpasses TiAl in resistance to oxidation and is light weight, so it is very interesting as a future material. The improvement of its plasticity has not yet progressed proportionate to the attention it is receiving as a practical material. But research is being conducted to improve its plasticity from the standpoint of alloy science. Its structure is of the tetragonal system based on an fcc lattice ($c/a \approx 2$), and the "ordered twin" is known to handle its deformation, as in the case of TiAl.

3. Other Intermetallic Compounds

Besides the abovementioned compounds, Ni₃Si and Ni₃Nb, which are regarded hopefully as new anticorrosive materials or as the main component phases thereof, and Co₃Ti, which is observed to be a component with great high-temperature strength and abundant cold plasticity, are included in intermetallic compounds as structural materials. The aluminides, silicides, and borides of high-melting-point metals are expected to receive growing attention hereafter as heat resistant materials that will be required by future technologies symbolized by the New Orient Express and the Japanese space shuttle concept, and research concerning their strength and plasticity are now beginning to be conducted.

4. Conclusion

To greatly advance intermetallic compounds and other new materials in the future, it is essential to develop the relationship between "basic research" and the "attempt to make something practical" whereby these "seeds" and "needs" each stimulate the other. In this symposium, the author will devote as much attention to this as possible and will refer to practical efforts as appropriate.

20108/9365

Alloy Design for Nickel-Base Superalloys, Titanium Alloys

43063804n Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 210-212

[Article by Toshihiro Yamagata, National Research Institute for Metals]

[Text] **Abstract:** The alloy design method constructed for conventionally cast nickel-base gamma-gamma prime type superalloys was effectively applied to development of nickel-base single crystal, superplastic P/M, and oxide dispersion strengthened superalloys.

For superplastic P/M alpha-beta titanium alloys, the alloy design method was established, and many alloys having high specific tensile strength, elongation, and good superplasticity were developed.

The targets of the project have been attained in single-crystal and ODS superalloys, as well as in P/M titanium alloys.

1. Introduction

In the research and development of advanced alloys with controlled crystalline structures, four alloy groups (Ni-base monocrystal alloys, Ni-base superplastic alloys, grain dispersion reinforced alloys, and Ti-base superplastic alloys) are objects of research and development, and the following development target performances surpassing the world level were set for each alloy group at the start of this project:

Monocrystal alloys: Must withstand stress of 14 kgf/mm² at the high temperature of 1,040°C for at least 1,000 hours and have rupture elongation of at least 10 percent at the time.

Ni-base superplastic alloys: Must have tensile strength of at least 160 kgf/mm² at the high temperature of 760°C and have ductility of at least 20 percent at the time.

Ti-base superplastic alloys: Must have specific strength of at least 28 kgf/mm²/g/cm³ at the high temperature of 300°C and have ductility of at least 10 percent at the time.

Grain dispersion reinforced alloys: Must withstand stress of 14 kgf/mm² at the high temperature of 1,100°C for over 1,000 hours and have rupture elongation of at least 5 percent at the time.

The National Research Institute for Metals is in charge of alloy design for alloy of these for groups based on a process appropriate to the characteristics of each alloy and satisfying their development target performances.

An Ni-base alloy basically is an alloy obtained through the precipitation hardening of the γ phase (Ni solid solution) by a γ' phase composed mainly of Ni₃Al. Normally, its crystal grain boundary is reinforced by adding C, B, Zr or Hf.

A monocrystal alloy is an alloy developed exclusively for monocrystal use in order to enable it to demonstrate its characteristics as an alloy. It is characterized by the fact that it never contains a grain boundary reinforcing element and that the coagulated structure is completely solution-annealed. It is an alloy for jet engine turbine rotor blades.

An Ni-base superplastic alloy is a powder-metallurgy alloy developed to manufacture gas turbine disks and other large members with a high working yield. It must have superplastic forgeability and high-temperature tensile characteristics.

A Ti-base superplastic alloy has two phases-- α phase and β phase--and is used to manufacture gas turbine compressor disks and other large members with a high working yield. It must have excellent superplastic workability and high specific strength.

A grain dispersion reinforced alloy is an Ni-base heat resistant alloy obtained by making Y₂O₃ grains, element powder and alloy powder mechanically into an alloy. It is characterized by the fact that it receives unidirectional recrystallizing heat treatment and is used in the columnar state. It is an alloy for jet engine turbine rotor blades.

2. Basic Concept of Alloy Designing

The alloy designing discussed here concerns how to design alloys in the area where the γ and γ' phases in the case of the Ni base and the α and β phases in the case of the Ti base coexist. In this situation, these phases are mutually balanced and each is solid solution hardened, but the components are adjusted so that a harmful phase will not be deposited and the phase may conform to its purpose. In other words, the principles of alloy designing for both phases are common and as follows (phases in parentheses are for Ti alloys):

- (1) Any composition of γ' (β) phase is assumed under the condition that it is balanced with γ (α) phase.

(2) The composition of γ (α) phase is calculated from the above composition of γ' (β) phase, using the ratio of distribution to γ (α) phase of each element and its γ' (β) phase.

(3) A check is made to see if a harmful phase σ (α_2) is deposited from γ (α) phase.

(4) Using the above compositions of γ' and γ (β and α), various alloys with different volume rates of γ' (β) phase can be designed without changing these compositions.

An equation for a γ' (β) plane where Al concentration is obtained as a function for elements other than Ni (Ti), using the composition of the γ' (β) phase in the actual alloy, is used to obtain a γ' (β) phase that can be balanced with the γ (α) phase. The distribution ratio of the elements is obtained by multiple regression analysis as the function for γ' composition from the measured values of compositions of γ' (β) and γ (α) phases.

γ' plane equation (at%)

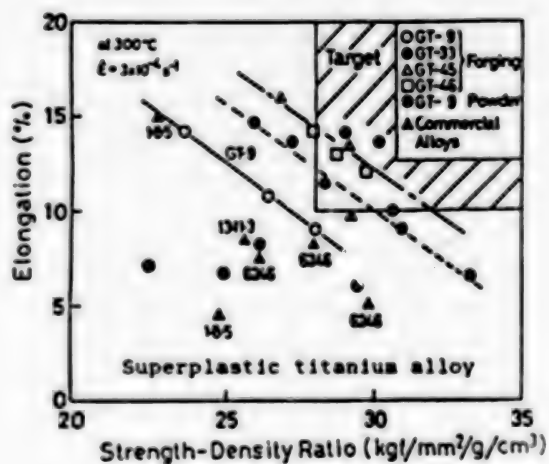
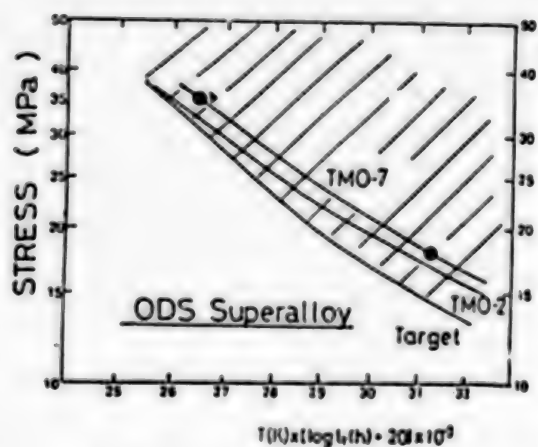
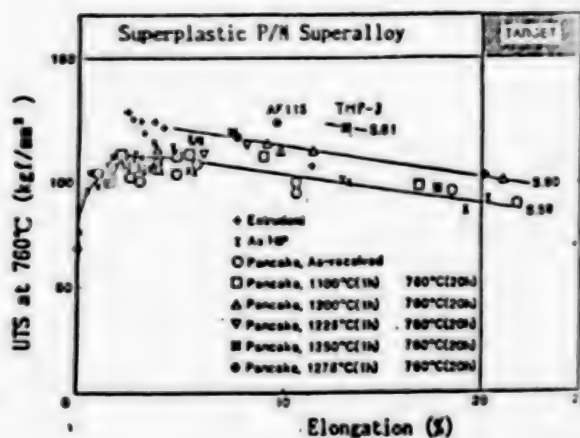
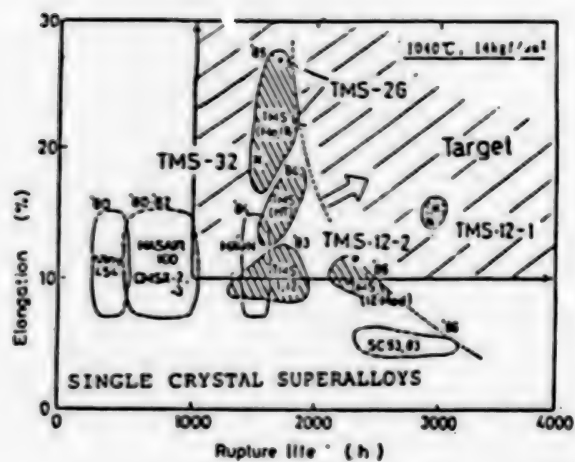
$$\text{Al} = 29.203 - 1.096\text{Cr} - 1.195\text{W} - 1.220\text{Ti} - 1.066\text{Al} \\ - 1.950\text{Mo} - 1.446\text{Nb}$$

β plane equation (at%)

$$\text{Al} = 2.192 + 0.17\text{V} + 0.4682\text{r} + 2.078\text{Mo} + 1.891\text{Cr} + 1.271\text{Fe}$$

3. Characteristics of Alloys Developed

In regard to monocrystal alloys, many with excellent characteristics, as indicated in the accompanying graphs, have been developed by alloy design with emphasis on the degree of solid solution hardening of the γ' phase and the ratio between Ta and W. In regard to Ni-base superplastic alloys, γ' quantities suitable for the working process have been ascertained and a study has been made on how such factors as composition, quantity of grain boundary reinforcing elements, and heat-treatment conditions affect their high-temperature characteristics. As can be seen from the graphs, characteristics better than those of AF15, the strongest alloy now in existence, are being obtained. In regard to grain dispersion reinforced alloys, the effect of γ' quantity on strength characteristics has been ascertained, using 1.1 wt% for 18 nm yttria powder and a constant γ' reinforcement quantity; alloy TMO-7 (Ni-9.2Co - 5.1Cr - 1.7Mo - 12.0W - 4.9Al - 1.0Ti - 5.4Ta - 0.05Zr - 0.05C - 0.01B - 1.1 (wt%)) far surpassing the target performance, as shown in the graphs, has been obtained. Ti-base superplastic alloys: the superplastic working temperature at which optimum superplastic characteristics can be obtained and the effect of β stabilizing element quantity on strength characteristics have been ascertained, and many alloys with performance better than the target, as shown in the graphs, have been developed.



Target of Jisedai Project and Results Obtained in Designed Alloys

20108/9365

Development of Ceramic Core for Gas Turbine Blade

43063804o Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 213-215

[Article by Yoshihiko Nozaki, Government Industrial Research Institute, Nagoya]

[Text] **Abstract:** There are various casting plans for single-crystal casting. The mold and the core must withstand thermal effects during the crystal growth. The development of the injection molding ceramic core for single-crystal turbine blades to improve the power of the gas-turbine engine is proceeding.

1. Gas Turbine Blade

The study of single-crystal casting technology under the Jisedai" (Next-Generation) Industrial Foundation Research and Development system consists of developing a high-efficiency gas turbine engine blade as an SC (single-crystal) cast blade. The first-stage rotor blade (Figure 1) for the gas turbine engine designated by the Jisedai Metal and Composite Material Research and Development Association is part of the structure to air-cool the interior of the blade. It is possible to make the interior of the blade hollow by using a ceramic core. A complex circuit is often designed for the cooling formula in order to improve the performance of the engine, and for this reason, the shape of the core is also complex.

This institute is in charge of conducting basic research on a ceramic core for single crystal use as part of the study of ceramic molds in precision casting included in research on single-crystal casting technology, and it is also in charge of the study to manufacture a core (Figure 2) for the first-stage rotor blade of the gas turbine designated. Laboratory-made ceramic cores continue to be supplied to the Jisedai Association, and evaluation tests in SC casting are commissioned to related private organizations. Figure 3 [not reproduced] shows the cross sections of a ceramic mold that was trial-manufactured.

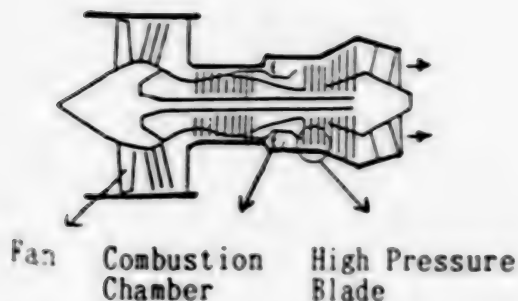


Figure 1. Gas-Turbine Engine

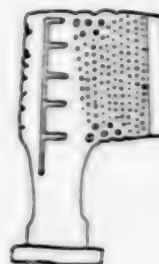


Figure 2. Ceramic Core

2. Ceramic Core for Single-Crystal Use

The target-shape core must have sintering-time size precision of less than 2 percent, casting-time ($1,600^{\circ}\text{C}$; about 2 hours) contraction and deformation of less than 2 percent, freedom from reaction to the developed alloy, freedom from blade damage after casting, and it must be capable of being removed by melting.

To achieve a ceramic structure that can withstand single-crystal casting, high-purity melted silica, a sealant for IC and LSI electronic components, is used as the main material by way of a countermeasure against reaction to metals, rather than melted silica for general casting. Its purity is at least 99.8 percent for SiO_2 , 250-2,500 ppm for Al_2O_3 , less than 50 ppm for Fe_2O_3 , and less than 30 ppm for MgO , TiO_2 , etc. To obtain thermal shock resistance in casting, silica crystallization is held to less than 10 percent, and the balance is of amorphous structure. Granular composition and the addition of a crystalline oxide are effective for overall accuracy. In this case, such SiO_2 oxides as silimanite and cristobalite are added in the amount of 5-30 percent. When using a nonsilica crystalline oxide, it must be added only in an amount permitting elution.

3. Manufacture of Ceramic Core

The core to be manufactured has the shape shown in Figure 2. Its shape is complex with a very thin (0.5 mm) fin tip and more than 150 $1.0\text{ mm}\phi$ pores. The manufacture of such a core was considered difficult by means of casting, pressing, and extrusion molding, which had been made practical in the ceramics-related industry, and then the injection molding of ceramics was developed (FY 1984 research results report). Thus core manufacture and supply, which has been considered a most difficult aspect of this research, was made possible.

3.1 Injection Molding of Ceramics

In the injection molding of ceramics and other powders, ceramic powder is injected into a metal mold via a nozzle by melting and fluidizing the binder additive and pressurizing it, rather than melting and fluidizing the powder itself; it is cooled and hardened and then removed from the mold as a molded product.

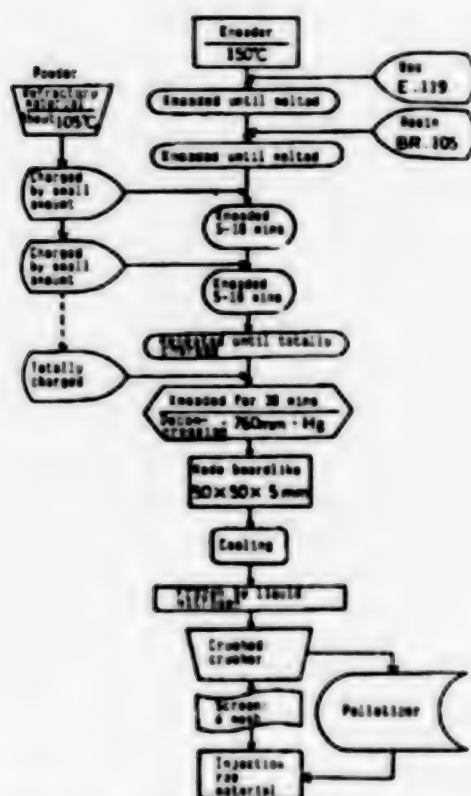


Figure 4. The Pelletizing Process

The injection molder used at the laboratory is a machine for resins in general, so the ceramic material must be pelletized (grains of about 3 mm), as in resin molding. Methods that have been developed to date for raw material adjustment and pelletizing are as shown in Figures 4 and 5 [latter not reproduced]. The pelletizing operation is as indicated in Figure 4. The freeze pulverizing by liquid nitrogen is an important process. For the injection molding of powder, the injection raw material is made by the procedure indicated in Figure 5, since the series of devices to pelletize by mixing powder with a binder for satisfactory dispersion are not on the market. The binder used is a 1:1 mixture of a wax having a melting point of 75°C and a viscosity of 100 cps (100°C) with a thermoplastic resin (methacrylate having a molecular weight of less than 55,000). The whole procedure is as shown in Figure 6. Figure 7 shows the mechanism of the injection molding; the present structure is indicated with solid lines. In the injection molding of ceramic and other powders, the pelletizing of raw material, the designing of the metal mold, and the burning of moldings are most important. Increasing the amount of binder used is impracticable, considering the accuracy of the core. At present, the amount added is 20 percent of the aggregate weight. The molding can be performed at injection pressure of 1,000 kg/cm² and cylinder temperature of 150°C. The degreasing of this core is completed in about 100 hours, and the core is then burned. Figure 8 [not reproduced] shows a metal mold developed for ceramic use and Figure 9 [not reproduced] shows its cores. In Figure 9, the core on the

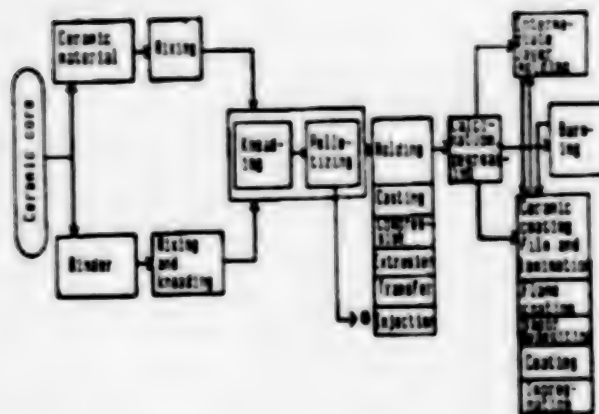


Figure 6. Ceramic Core Producing Process

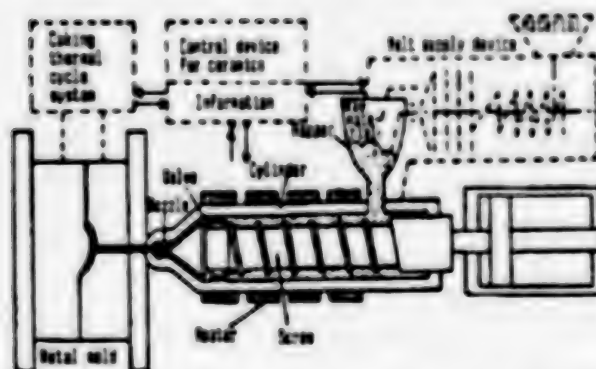


Figure 7. Mechanism for Injecting Molding for Ceramic Powder

right is in the state prior to degreasing, with a gate severed after injection molding; one can see by comparing it with the burned core on the left that there is hardly any difference in size.

Injection molding is suitable for cores because by this method complex shapes can be molded without variation in moldings.

20108/9365

Single-Crystal Casting, Performance of New Superalloys

43063804p Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 216-218

[Article by Shinichi Ohama, Ishikawajima-Harima Heavy Industries Co., Ltd.: "Single-Crystal Casting and Characterization of Advanced Superalloys"]

[Text] **Abstract:** Research and development of single-crystal superalloys for gas turbine applications have been carried out under the management of the Institute of Metals and Composites as a Japanese government-sponsored program. This paper summarizes the current status of the casting technology development to obtain cleaner metals, higher temperature gradient at solidification, and process automation, which result in improvement of the casting quality and the rejection rate. The solidification was simulated based on the heat transfer calculations of thermal radiation, giving useful information on the experiments. Various physical and mechanical properties of the newly developed alloys were evaluated, confirming, for instance, excellent creep rupture strength well exceeding the objective strength level.

1. Introduction

Research and development to improve the heat resistant temperature of high-pressure turbine members is being actively conducted, because in jet engines and industrial gas turbine, turbine inlet temperature is a factor directly determining performance and efficiency.

In Japan, the development of superalloys for single-crystal casting and the development of the technology to manufacture single-crystal castings are being carried out as a theme of developing advanced alloys with controlled crystalline structures commissioned under the Jisedai (Next-Generation) Industrial Foundation Research and Development System. In this area, Daido Special Steel is in charge of development of ingot technology of melting stocks for casting. Hitachi, Ltd., and Ishikawajima-Harima Heavy Industries Co., Ltd., are in charge of development of the technology to manufacture single-crystal castings, and they are also conducting evaluation tests, comprised mainly of casting and creep tests on alloys developed by the National Research Institute for Metals and casting tests on molds and cores developed by the Government Industrial Research Institute, Nagoya.

The present state and characteristics of development of superalloy single-crystal castings manufacturing technology are outlined here on the basis of the results of these tests.

2. Technology of Manufacturing Single-Crystal Castings

The development of superalloy single-crystal castings began with the casting of round bars or test pieces, advanced to the trial manufacture of rotor blades modeled in a two-dimensional shape with cooling holes (referred to as intermediate configuration), and in the final stage, cooling turbine rotor blades in the actual shape are being trial-manufactured.

2.1 Development of Coagulation Control Technology

Coagulation control is important to the manufacture of superior superalloy single-crystal castings. The purposes of coagulation control include:

- 1) making complete single crystals without generating superfluous crystals;
- 2) avoiding the generation of casting defects, including porosity;
- 3) making crystal orientation uniform in the target direction;
- 4) refining the arborescent structure;
- 5) speeding up production; and
- 6) improving yield.

To accomplish these goals through coagulation control, it is necessary to develop the technology for such purposes as: 1) increasing the temperature gradient on the coagulation interface; 2) making the coagulation interface flat or convex; 3) making the mold-lowering speed (crystal-growing speed) as high as possible; and 4) selecting and developing crystal nuclei in the target bearing. The conditions for each must be established by the technology.

This research and development is aimed primarily at clarifying the technology of coagulation control and attaining the targets by a rational approach that comprises more than just the accumulation of experiences.

2.1.1 Coagulation Analysis and Computer Simulation of Coagulation

If it is important to control the shape of the coagulation interface and its temperature gradient, clarifying the process of coagulation and making computer simulation of coagulation not only provides an effective means of research but will also enable coagulation to be computer-controlled in actual manufacturing.

Superalloy single-crystals normally are manufactured in a vacuum by the mold lowering method. Since the heat absorption and desorption in the vacuum coagulation process are governed by radiant heat transfer, we used the NASTRAN program to calculate radiant heat transfer. We first determined a radiation form coefficient from the geometric shape correlation between the heating furnace and the mold by the VUFACT program, and using this, calculated heat transfer by the SINDA program. We handled calculation by the internal nodal point method, and coagulation latent heat

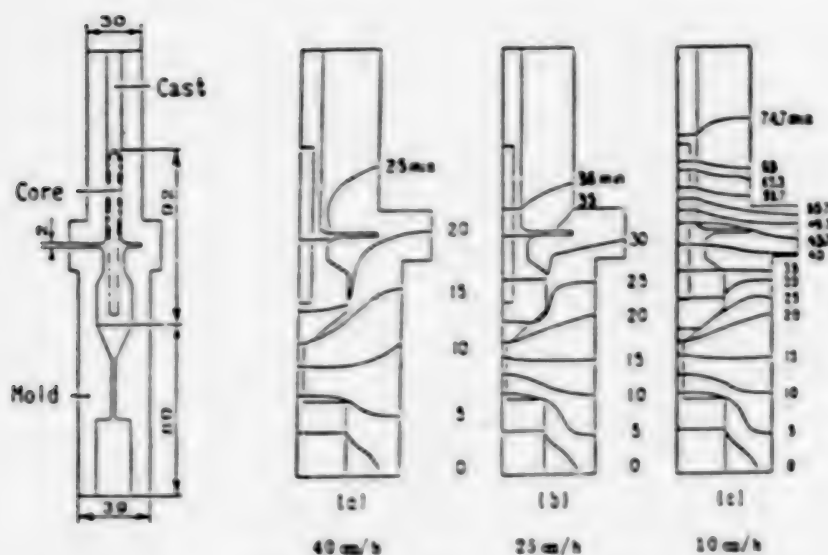


Figure 1. Blade Model and Iso-solidus Line Transition Obtained for the Blade Model

by the equivalent specific heat method. Figure 1 shows the secular change of the solid-phase line at the time of changed mold lowering speed as an example of coagulation simulation. At (a) and (b) lowering speeds, the coagulation interface is convex downward, hinting at the prospect of nuclei generation at the place where the cross section changes, but if a slow lowering speed is used, as in (c), the coagulation interface is flat, hinting at the prospective possibility of monocrystallization.

2.1.2 Computer Control of Coagulation

The stability of the coagulation interface has been shown to be important as the result of coagulation analysis. The coagulation interface depends on the ratio between temperature gradient G and coagulation speed R . $G/R > 1^\circ\text{C}\cdot\text{h}/\text{cm}^2$ is necessary to maintain a satisfactory state of unidirectional coagulation, but the use of a computer has made possible control by changing R in accordance with the change of G .

2.1.3 Control of Crystal Orientation

It is known that the preferential growth bearing at the time of coagulation of face-centered cubic crystals, such as Ni-base alloy, is $\langle 100 \rangle$. The fact that strength in this bearing is highest is a decided advantage in applying single-crystal alloys. The accuracy and probability by which this bearing can be obtained is believed to be related to such factors as the shape of the crystal starter, the shape of the selector and the casting temperature, and the technology to control these has been established.

2.2 Trial-Manufacture of New Superalloy Single-Crystal Castings

Figure 2 provides an outline of the furnace to be used to train-manufacture and test superalloy single-crystal castings. The mold is heated by a

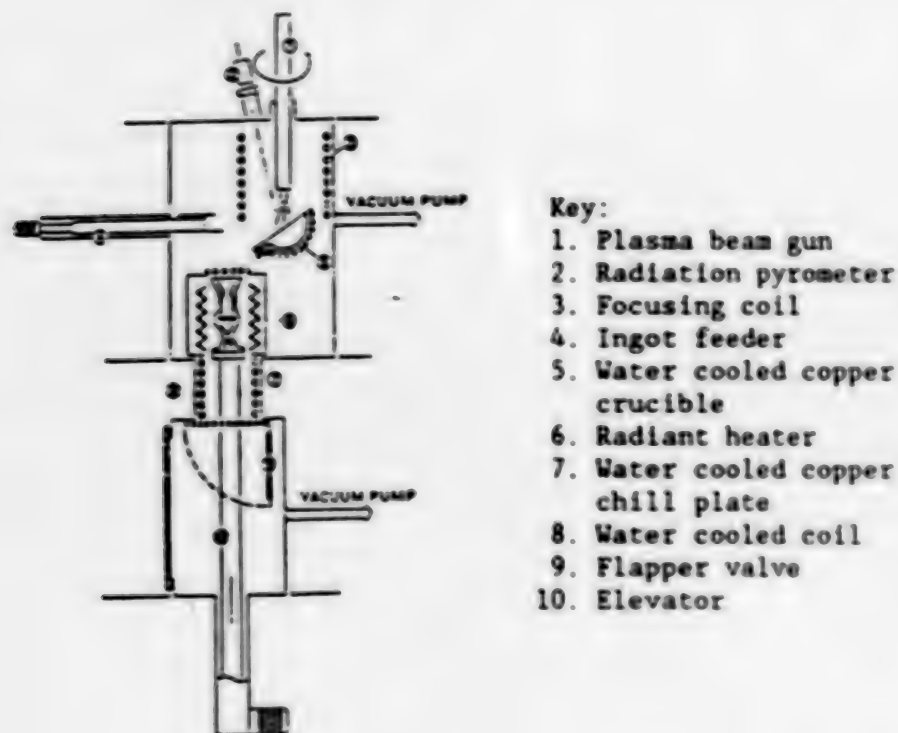


Figure 2. Schematic Structure of IHI-MIZUHO Single-Crystal Casting Unit

resistance heater with an inner diameter of $\phi 200$ mm and divided into two parts--top and bottom--and G of some $60\text{--}80^\circ\text{C}/\text{cm}$ is obtained. For melting, 300 kW plasma beam skull melt is used and the series of operations including melting and lowering is performed automatically by computer.

When the trial-manufacture of intermediate configuration and actual shape turbine rotor blades was carried out by this experimental furnace, the results generally agreed with the results of coagulation simulation, thus revealing that single crystallization of new superalloys is possible. There are, however, problems to be solved, including countermeasures against some casting defects and the setting of optimum conditions for manufacturing.

3. Characteristics of New Superalloy Single-Crystal Castings

The target value of strength in this research and development project is a creep rupture life of at least 1,000 hours at $1,040^\circ\text{C}$ and $14\text{ kgf}/\text{mm}^2$. The new superalloy fully satisfies this target value, and, as indicated in Figure 3, exceeds the existing alloys at all test temperatures. We also tested its physical properties, high-temperature tension, and fatigue.

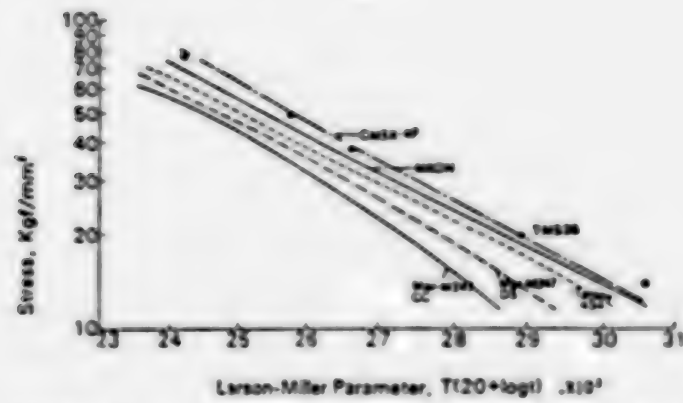


Figure 3. Larson-Miller Parameter Curve Comparing Stress Rupture Lives of Single-Crystal Alloys With Directionally Solidified Alloy (DS)

20108/9365

Process, Properties of Nickel-Base ODS Alloy TMO-2

43063804q Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 219-221

[Article by Yoshinobu Takeda, Sumitomo Electric Industries, Ltd.]

[Text] **Abstract:** Ni-base ODS alloys became one of the most important materials used for turbine engine components because of their outstanding heat resistant property. The heat resistant property of Ni-base ODS alloy is primarily due to uniformly dispersed fine yttria particles as strengthening dispersoids. The alloys are manufactured by new powder metallurgical processes such as mechanical alloying (MA) and powder extrusion. In a project of Basic Research for Future Technologies supported by the Institute of Technology, MITI, the new processes have been established and a newly designed ODS alloy TMO-2 has been successfully developed.

This work describes the details of the MA and powder extrusion processes. 1) A homogenizing process during MA has been analyzed by EPMA and XRD (X-ray diffraction). Milled raw powder particles were found within each particle processed for a short period of 5 hours. On the other hand, there was no discriminative deviation of alloying elements within each particle processed for a sufficient period of 50 hours. XRD showed a decrease in the peak intensity of the W and Mo added as elemental powders, which suggests the promotion of the alloying. 2) The recrystallization behavior of the materials extruded at different reduction ratios was investigated. A reduction ratio higher than 16 was found to be necessary to obtain enough grain coarsening to get creep resistance. Based on the results of these investigations, a bar of 40 mm diameter of TMO-2 with good grain coarsening property was obtained.

1. Introduction

Ni-base ODS alloys excel in high-temperature heat resistance and anticorrosiveness. MA6000, for instance, which is an Ni-base ODS alloy presently on sale, has high-temperature strength better than that of Ni-base single-crystal alloys. The superior heat resistance of Ni-base ODS alloys is due to oxide particles (Y_2O_3) being finely dispersed in them for strengthening. In the Jisedai Industrial Foundation Technologies Project

of the Agency of Industrial Science and Technology, NITEL, are included: mechanical alloying which is the basic technology to make this version of this oxide and basic technology to disperse these oxide particles. At the same time the new alloy TMO-2 was developed. This article describes the extrusion technology which is the MA and particle formation and solidification process.

2. ODS Alloy Manufacturing Process

As indicated in Figure 1, the MA process consists of taking various raw material powders mixed so as to attain a target composition and putting them into a processing tank for high-energy ball mill called (attriter) and performing forced mixing of these with steel balls. The composition of TMO-2 is Ni-5.9Cr-9.7Co-12.4W-2.0Mo-4.7Ta-0.8Ti-4.2Al-0.05Zr-0.05C-0.01B-1.1Y₂O₃. By means of MA, the powders repeatedly collide with the steel balls, and in the process, the various raw material powders are mixed together and, during repeated reconstitution and pulverization, the individual independent particles form alloy powder having the target composition. The powder having been mechanically alloyed is vacuum-sealed in a soft steel sheath, and after undergoing hot extrusion at 1,000°C or more, it is thermally treated and provided for use.

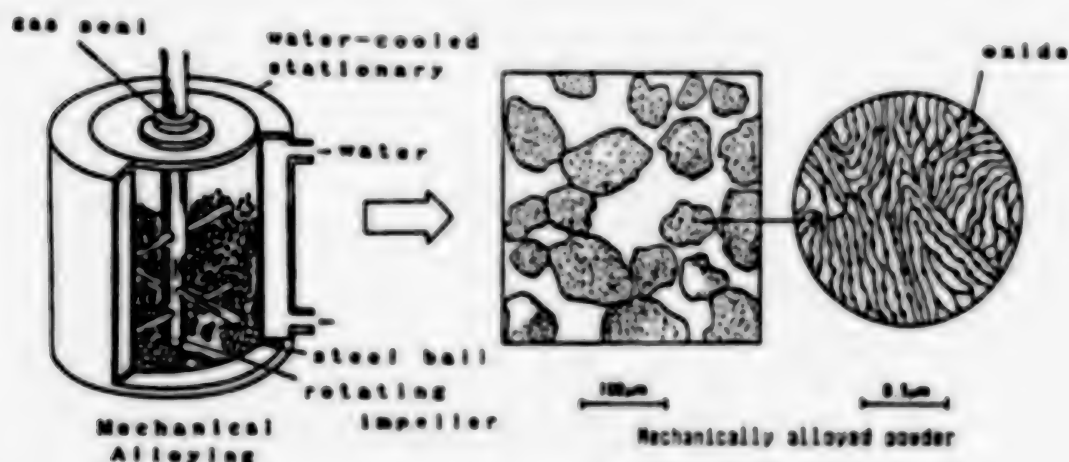


Figure 1. Method of Mechanical Alloying

3. Manufacture of ODS Alloys and Evaluation of Material Characteristics

3.1 MA and Mechanically Alloyed Powder Characteristics

MA was conducted by the turning of an agitator at a rotational speed of 200 rpm in an Ar gas atmosphere for 50 hours. By means of MA, the various raw material powders are mixed together and become increasingly homogenized, and in the meantime, various changes take place in the powders. Their hardness suddenly increases at the beginning of MA, and in about 30 hours, it attains 850 mHv and becomes constant there. The powders become fine and then coarsen. Figure 2 [not reproduced] shows the results of an investigation--made by EPMA line analysis of mechanically alloyed powder--into the progress of alloying, which is the most important change.

After a treating time of only 5 hours, each raw material powder was observed in an unalloyed state, but after 50 hours of treatment, the raw material powders had mixed so well that they could hardly be discerned by EPMA analysis, thus suggesting the progress of alloying. The extent of alloying can also be determined by X-ray diffraction. It was learned that, as shown in Figure 3, the diffraction peaks of Mo and W decreased with the progress of alloying.

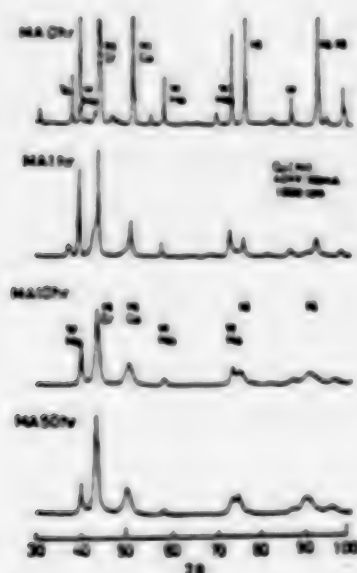


Figure 3. Change of X-Ray Diffraction Pattern of MA Powders During Mechanical Alloying

3.2 Extrusion and Recrystallization Characteristics of Extruded Materials

Mechanically alloyed powder was vacuum-sealed in a soft steel can at 500°C and then molded by hot extrusion at 1,050-1,100°C. The extrusion ratio at the time was 10-16 and the extruding speed was 400 mm/sec. This extrusion is not just meant to mold and solidify the powder but it is also a process to provide the working strain necessary for unidirectional recrystallization in the subsequent heat treatment. That is, an extruded material must have its crystal grains coarsened in one direction in order to increase its heat resistant strength, particularly its creep strength, but its recrystallinity is poor, and target cluster composition cannot be obtained unless sufficient working strain is provided at the time of extrusion. Figure 4 shows the results of an investigation into the recrystallinity of ϕ 40 to ϕ 50 extruded materials extruded by various extrusion ratios at 1,100°C. Crystal coarsening after annealing was possible for material that had a high extrusion ratio and hardness of only about 500 mHv after stationary annealing, but material that had a small extrusion ratio was hard even after annealing and its recrystallinity was poor. But now, we have succeeded in obtaining a material with high ϕ 40 recrystallinity. Figure 5 [not reproduced] is an optical microscope photograph of crystal grain coarsening composition obtained by stationary annealing.

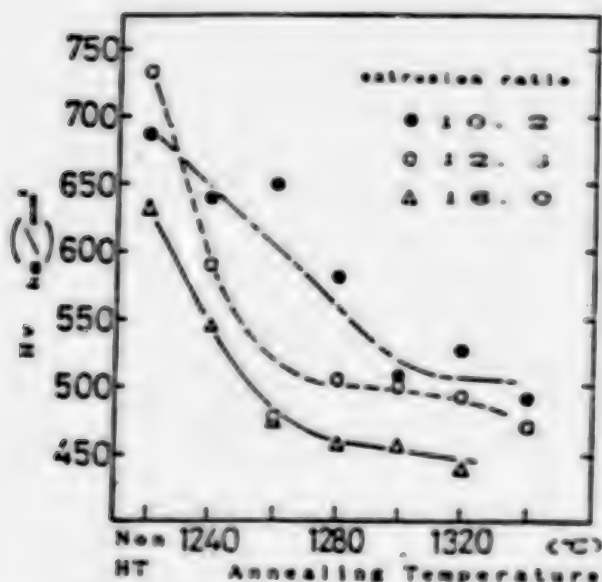


Figure 4. Microhardness as a Function of Annealing Temperature for Extruded TMO-2 (Annealing time: 1 hr)

4. Conclusion

We have seen above the material characteristics of Ni-base ODS alloys by means of MA and extrusion. Regarding the creep characteristic of TMO-2 alloy prepared thus, it has been confirmed that this alloy has a life of 3,210 hours (project target value: 1,000 hours) under the conditions of 1,050°C and 16 kg/mm². This company is planning to study the reproducibility and reliability of its heat resistant strength characteristic.

20109/9365

Melt-Spun Nickel-Base Superalloy Ribbons

43063804r Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 222-224

[Article by Ken Yasuda, Hitachi Research Laboratory, Hitachi, Ltd.: "Application and Superplasticity of Melt-Spun Ni-Base Superalloy Ribbons"]

[Text] **Abstract:** Fine grain Ni-base superalloys are expected to exhibit microstructural and mechanical property improvements. The purpose of the present study is to produce fine-grained Ni-base superalloy ribbons by the double roller quenching method, and to investigate the superplasticity of ribbons as well as the application of ribbons to solid phase diffusion welding for Ni-base superalloy as an insert metal. The main results obtained are as follows:

- (1) The n values of ribbons are found to be more than 0.3.
- (2) The maximum elongation value of ribbons is larger than 360 percent, which is the limit of the test machine used.
- (3) The welding strength of Ni-base superalloy Rene-80 using ribbons is higher than that without ribbons under all welding conditions. This means that the ribbons contribute to the improvement of welding strength, and this effect is due to easily deformable ribbons with small grains.

1. Introduction

Developing new materials and processes promising technological advance is becoming increasingly important. One of these new materials and processes concerns new materials development and process research using rapid liquid coagulation. The effects of rapid liquid coagulation include: 1) refining of crystal grains; 2) formation of a nonequilibrium phase; 3) extension of solid solution limits; and 4) refining of a deposition phase. Rapid liquid coagulation materials are normally prepared in ribbon form or as a powder because of the necessity to improve their coagulation speed.

Meanwhile, Ni-base superalloys used as heat resistant alloys for jet engine and gas turbine blades have greater high-temperature strength than that of any other metallic material, but they cannot be plastically worked by

forging or other means because of their great strength, so products are made of them by precision casting. New characteristics, such as the possibility of plastic working by the appearance of fine crystal grain superplasticity, can be expected of the refining of Ni-base superalloy crystal grains by rapid liquid coagulation, and this technology bids fair to develop as a next-generation industrial foundation technology. Under the next-generation project, the author, et al., are conducting research into the characteristics of superalloy ribbons prepared by the double roll method and their industrial application. Here, we shall look into the use of superalloys as a superalloy joining insert material with a view to industrial application, taking advantage of the superplasticity phenomenon of superalloy ribbons and their shape.

2. Preparation of Superalloy Ribbon and Superplasticity Phenomenon

As typical ribbon making methods, there are the double roll method and the single roll method. This report concerns the double roll method of preparing ribbon, which characteristically excels in thickness homogeneity and has equal properties on both sides of the ribbon. Ribbons can be appropriately shaped by controlling the conditions of preparation; the shape in which the author, et al., normally prepare them comprises a width of 5-15 mm and a thickness of 50-150 μm . They are prepared in an inactive gas atmosphere because active elements, such as Al, Cr, Ti, and Nb, are contained in Ni-base superalloys.

The superplasticity phenomenon of Ni-base superalloys is being studied by means of a high-temperature tension test using varied rates of strain concerning Ni-Al-X (X = Cr, Ti, etc.) comprised of the principal components of Rene-80, IN738LC commercial alloy, TMP-3, which is an alloy to be developed under the next-generation project, and Ni-base superalloy. Each of these alloys has an area in which the rate of strain sensibility index shows a value of 0.3 or more, and in test piece elongation under suitable conditions, no rupture occurs even beyond 30 percent of the test equipment limits. The deformation resistance at 1,100°C is approximately 1 kgf/mm². Figure 1 shows the m-values of superalloy ribbons.

3. Superalloy Ribbon Application for Joining Insert Materials

As the present method for joining Ni-base superalloy, there is liquid phase diffused junction characterized by providing the joining plane with an Ni-B layer having a melting point lower than the melting point of the base material. This method is remarkable for its low junction stress, but because of the difference in the joint composition from the base material composition, it involves such problems as: 1) prolonged joint homogenization; 2) strength deterioration due to the formation of B compound and other different phases in the joint; and 3) in joining an oxide dispersion superalloy, agglomeration of dispersed particles by joint melting. But in solid phase diffused junction using an insert material composed approximate to the base material, these problems presumably can be solved. Here, the effect of suppressing base metal deformation and improving base metal adherence by the deformation of the insert material can be expected from the use of insert material. But in ordinary solid

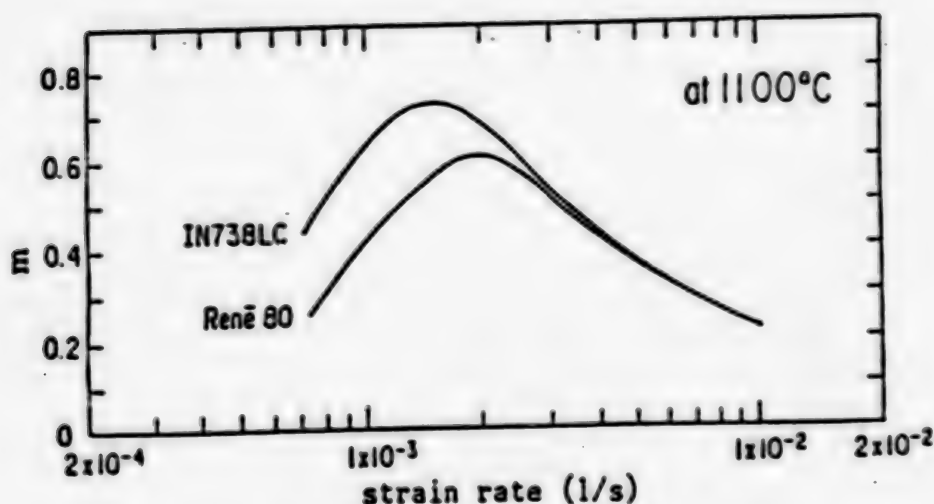


Figure 1. Correlation Between Strain Rate and M Value of Ni-Base Superalloy Ribbons

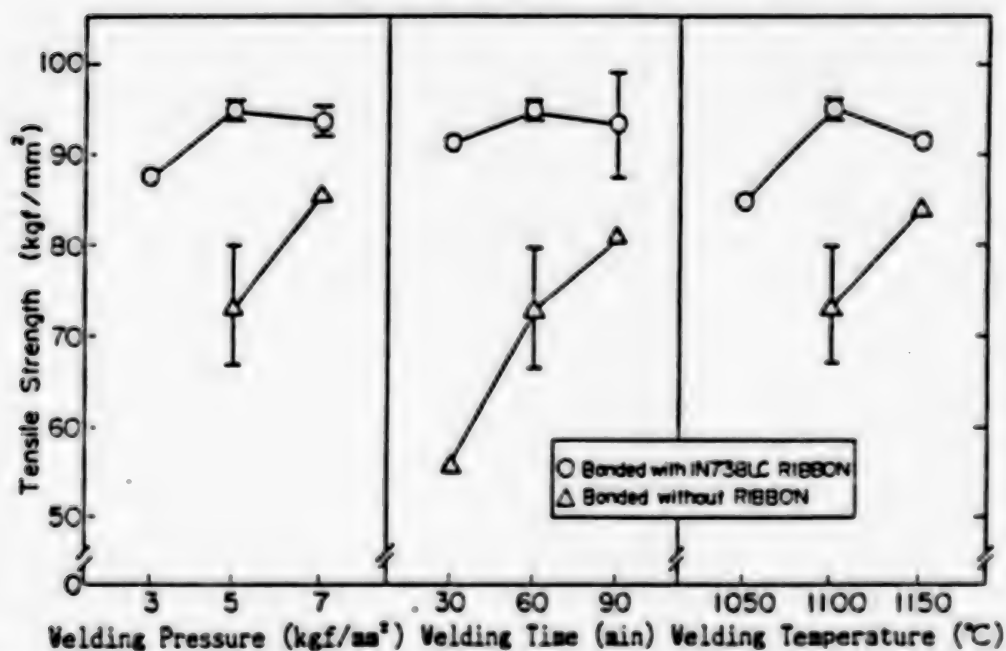


Figure 2. Correlation Between Welding Condition and Tensile Strength at Room Temperature
(Standard welding condition: welding pressure 5 kgf/mm², welding time 60 min, welding temperature 1,100°C)

phase junction, high junction stress is necessary. Also, working a γ -phase deposition-reinforced Ni-base superalloy into sheets, such as for use as junction insert material, is difficult.

These problems presumably can be solved if Ni-base superalloy ribbons with small deformation resistance are used as the insert material. Figure 2 shows the results (room-temperature tensile strength) of the study of junction strength comparing, on the one hand, a case wherein Rene-80 and

IN738LC ribbons were used as, respectively, base metal and insert material (joining conditions, stress, time, and temperature were varied; and ribbons were used as junction insert material) and, on the other hand, a case wherein pieces of base metal were directly joined without using junction insert material. Under either joining condition, the material that was joined using ribbons showed higher strength than the material joined without ribbons. Thus, it can be seen that ribbons contribute to improvement of joining strength. This means that the use of ribbons is effective in decreasing junction stress. These effects are due more or less to the ease with which insert material with small crystal grains is deformed. Furthermore, insert material fills base metal fissures even if the surface roughness of the base metal is as great as some 60 μm .

Here, the composition of insert material affects junction strength, so the joint can be strengthened by appropriately composing the insert material, and, in addition, base metal rupturing becomes possible.

4. Conclusion

It is hoped that the technology taking advantage of the characteristics and shape of Ni-base superalloy ribbons able to exhibit superplasticity and minimize deformation resistance will advance as a next-generation industrial foundation technology.

This research was conducted as part of the "research and development of advanced alloys with controlled crystalline structures" commissioned to the Jisedai (Next-Generation) Metals and Composite Materials Research and Development Association (a foundation) under the Jisedai Industrial Foundation Technological Research and Development System of the Agency of Industrial Science and Technology, MITI.

20108/9365

High Tc Superconductive Material Technology

43063804s Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 230-232

[Article by Takeshi Kobayashi, Faculty of Engineering Science, Osaka University: "High Tc Superconducting Material Technology and Its Application to New Electronics"]

[Text] **Abstract:** High Tc superconductor films were grown in several crystalline forms, e.g., (110) oriented epitaxial crystal, polycrystal, and polycrystal with c-axis preferential orientation. The film had critical temperature as high as 87 K. The microfabrication technique based on chemical wet etching by phosphoric acid and FELLIOX-115 was proposed. The thin line (2-4 μm wide) made thus, showed no sign of degradation in its superconductivity. A negatively biased ECR-plasma-oxidation greatly helped the oxygen filling in the high Tc superconductor materials. The grain boundary in the patterned polycrystalline film served as a good Josephson junction operative at 81 K. A constricted Josephson junction array device was fabricated for use as a sensitive image sensor. A three-terminal high Tc superconducting transistor with injection gate was fabricated, but current gain has not been achieved yet. A possible application of ErBaCuO system to the luminescence device has been studied.

1. Preparation of High-Temperature Superconductive Films

We prepare Y-Ba-Cu-O and Er-Ba-Cu-O compound superconductive films. These films are formed on (110) and (100) SrTiO_3 substrates and YSZ ceramic substrates by rf diode magnetron sputtering. We are also studying film formation by means of the plasma CVD-sputter hybrid formula using HFA organic metal gas.

A (110) YBaCuO as-grown epitaxial film on a (110) SrTiO_3 substrate was obtained by the magnetron sputtering of (Ar and O_2) mixed atmosphere (Figure 1(a)). The epitaxial state was also confirmed by RHEED observation. But there is lengthy disturbance of the three-layer perovskite structure, and stoichiometrical adjustment of the (1-2-3) composition is absolutely necessary to solve this problem. Stoichiometrical adjustment similar to the preparation of semiconductor crystals will be undertaken in the future.

2. High-Temperature Superconductive Film Working Technology

We developed a method of wet chemical etching, a simple microfabrication technique applicable to polycrystal membranes. We also elucidated the relationship between acceleration energy and crystal deterioration with respect to the ion process for supermicrofabrication. The process for a line width of about 2 μm in polycrystal membrane can be easily performed using phosphoric acid: FELLIIX-115 (Figure 2). In the wet chemical etching method, ErBaCuO etching speed is double, compared with YBaCuO (Figure 3). Changes in the value of the Cu ion at the time the surface of YBaCuO was irradiated with Ar ion were ascertained by ESCA analysis. Figure 4 indicates that the peak is maintained at bivalence in the case of acceleration ion irradiation at less than 1 kV, but beyond that level, the value shifts to the monovalent side. Thus, the upper limit of acceleration energy in ion beam working has proved to be 1 keV. Oxygen filling for the Cu-O one-dimensional chain was carried out by ECR microwave plasma oxidation. Oxidation was greatly accelerated by negative bias impression (Figure 5).

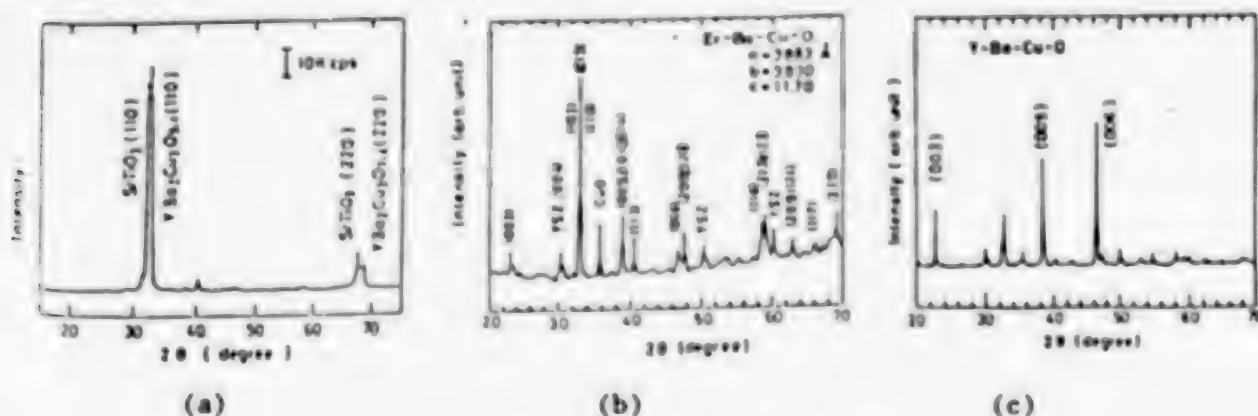


Figure 1. X-Ray Diffraction Patterns
(a) (110) epitaxial crystal
(b) Polycrystal
(c) Polycrystal with (100) preferential orientation

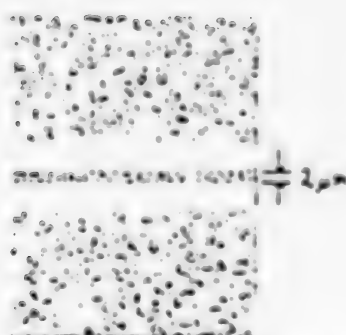


Figure 2. Thin Line Etched With FELLIIX-115

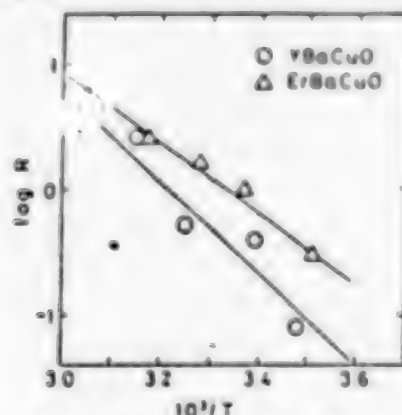


Figure 3. Etching Rate Vs Temperature. FELLIIX-115

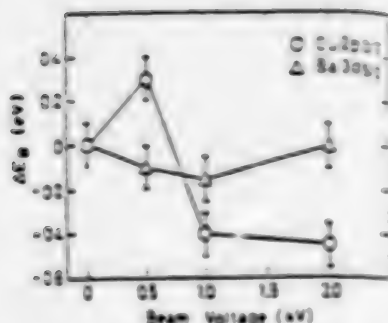


Figure 4. Shift of ESCA Peak Energy Due to Ar-Ion Irradiation

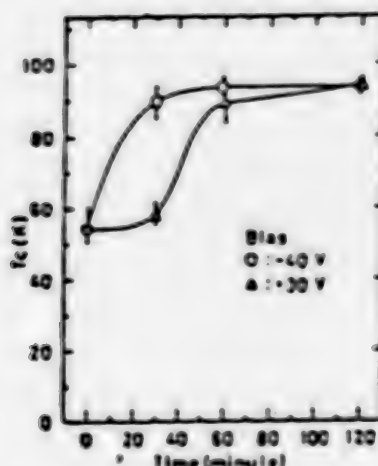


Figure 5. ECR Plasma Oxidation Under DC Bias Stressed

3. Application of High-Temperature Superconductive Materials to Electronics

This material has many applications to electronics, starting with such simple items as a Josephson junction device composed of two terminals, and including innumerable items such as a three-terminal transistor with control electrodes, a super-high-efficiency transistor (super-HET) based on semiconductor/superconductor junction, a super-OEIC with a light emitting/receiving section taking advantage of properties peculiar to high-temperature superconductive materials, and a low-dimensional conduction element. High-temperature superconductive material was developed only recently, but it is already beginning to be used as a definite device; it is a fascinating new material.

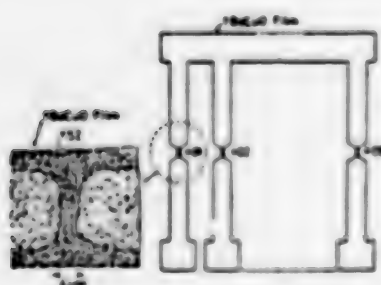


Figure 6. Linear-Arrayed High-Tc Image Sensor Device

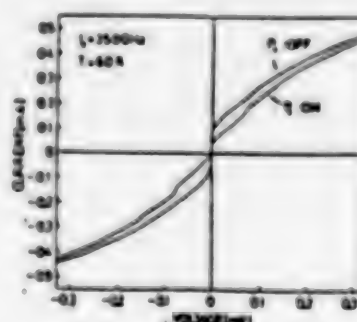


Figure 7. Millimeter-Wave Response of the Grain-Boundary Josephson Junction

Figure 6 shows a high-temperature superconductive image sensor comprised of a linear array of boundary Josephson junction. Figure 7 shows how it responds to 35 GHz electromagnetic waves. This element operated all the way up to 81 K. It is hoped that this material can be made into a super-low-noise biosensor. A three-terminal transistor of the quasiparticle

injection type was trial-manufactured for the first time (Figure 8). Although it has not yet produced current gain, it is considered likely to produce considerable gain as a result of structure optimization. Figure 9 shows a PL spectrum taking advantage of the 4f electron light emission transition of Er atoms. A light emitting element of the injection type may be developed in the future that will provide a powerful means to evaluate crystallinity, as well as being used as a device.

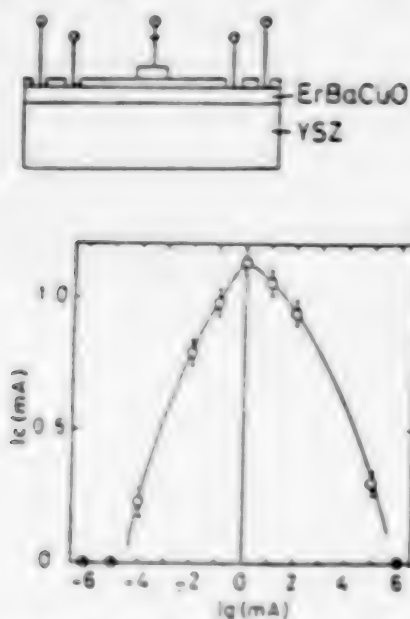


Figure 8. Three-Terminal Transistor With Quasiparticle Injector

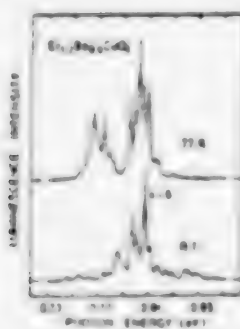


Figure 9. Photoluminescence From ErBaCuO Ceramics

20108/9365

Critical Current Characteristics in High Tc Superconductors

43063804t Kobe INTERNATIONAL SYMPOSIUM ON BASIC TECHNOLOGIES FOR FUTURE INDUSTRIES, MATERIAL DEVELOPMENT AND INNOVATION in Japanese 22-25 Mar 88 pp 237-240

[Article by Teruo Matsushita, Faculty of Engineering, Kyushu University]

[Text] **Abstract:** Critical current density is a key parameter for application of high Tc oxide superconductors. Its values in sintered ceramics or powder-processed wires reported so far are very low, although inductive measurements clarify that the density of closed current flowing within grains is fairly high. This is caused by a percolative feature due to imperfections such as voids or insulating layers. The critical transport current density of these materials with randomly oriented grains are estimated by means of a percolation theory taking into account anisotropy in flux pinning structure. It is expected to be improved up to the intra-grain current density by improving the quality of materials. If a fine-grain structure of about 0.1 μm in diameter or an oriented structure of twinning planes is realized, the critical current density at 77K will reach the present level of commercial Nb-Ti.

1. Introduction

The discovery of an oxide superconductor with a critical temperature exceeding that of liquid nitrogen and an upper critical magnetic field, B_{c2} , higher than that of the conventional high-magnetic field superconductive material is a breakthrough that has drastically expanded the possibilities of engineering application of superconduction. Another important application characteristic is current density that can flow without loss, namely, critical current density, J_c . It has hitherto been reported that film and single-crystal specimens have considerable critical current density,¹ thus assuring a promising future for this material. But the values of critical current density obtained from sintered and other materials suitable for the mass production of superconductive wiring indispensable for use for electric power equipment, etc., are small. Furthermore, if there is a large current flowing in the crystal grains, it is closed and is known not to contribute to the transport current.² The improvement of this characteristic is therefore desired, but is this possible? If so, to what extent? In this article, I will make clear the present status of the YBaCuO sintered material and its problems, and I will

also discuss the level of critical current density that can be attained in the future.

2. Electromagnetic Phenomenon

Regarding the critical current of sintered bodies, observation has revealed that values obtained by the ordinary resistance method and those obtained from magnetization measurement greatly disagree, the degree of magnetization is out of proportion to the size of specimens and is almost constant, and there are other differences from the characteristics of conventional bulk superconductive materials. This indicates that screening current flows in the process of magnetization, but it does not flow uniformly to specimens; on the contrary, a considerable part of it flows enclosed in the grains. In fact, if penetration depth λ' of AC magnetic field is plotted against magnetic field amplitude b , using the method of micro AC magnetic field superimposition,³ the result is as shown in Figure 1. In ordinary bulk specimens, this gradient is $1/\mu_0 J_c$. This result indicates that small bulk current and large intra-grain current independent of it exist together. The density of this bulk current is much the same as that which can be obtained by the resistance method, and the value of the intra-grain current is nearly equal to the value obtained for the powder from magnetization measurement.⁴ The reason why locally flowing current, if there is any, does not contribute to the transport current is because the current path is intercepted by imperfections such as voids, ordinary conductive phase and insulating layer in crystal grains. It is therefore necessary to eliminate the ordinary conductive phase by increasing density as much as possible and realizing a state close to stoichiometry by homogenizing the composition.

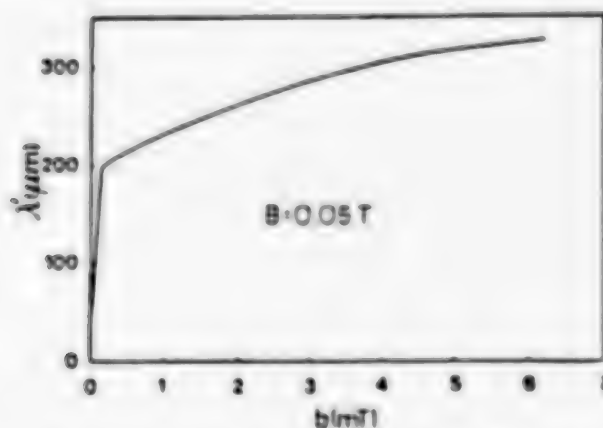


Figure 1. AC Penetration Depth λ' Vs AC Field Amplitude B
First abrupt flux penetration and second gradual one correspond to bulk and intra-grain currents, respectively.

3. Critical Transport Current Density

It is through the action of magnetic flux pinning to stop the motion of the quantization magnetic flux in opposition to the Lorentz force that DC

current can flow without electric resistance in the condition of a magnetic field. In the case of oxides, it is conceivable that the crystal grain interface and the twin planes have the action of magnetic flux pinning. The intensity of interaction consisting mainly of the pinning of these planes (elementary pinning force) is

$$\hat{f}_p = A \frac{B_c^2}{\mu_0} \xi_0 \left(1 - \frac{B}{B_{c2}}\right) \quad (1)$$

per unit length of the magnetic flux that is parallel to this.⁵ Here, A is a constant, B_c is a thermodynamic critical magnetic field, and ξ_0 is the length of coherence of BCS. At this time, the critical current density is given by

$$J_c = \frac{k \hat{f}_p}{B a_f d} \quad (2)$$

Here, k is a constant, a_f is a magnetic flux lattice interval, and d is a pin interval (in the case of a crystal grain interface, a crystal grain size). The accurate values of A and k have not yet been obtained, but it is empirically known from past examples of high magnetic field materials that $Ak \sim 0.2$ can be used. In Figure 2, critical current densities at 77K and 4.2 K obtained thus are shown, together with the results for conventional materials.⁵ Here, $d = 0.2 \mu\text{m}$ is assumed, and the structure used is either isotropic crystal grain structure of this size or structure wherein twinning plane is arranged at this interval and vertical to the Lorentz force. It is expected that in this state, characteristics comparable to those of the present Nb-Ti can be obtained at 77 K.

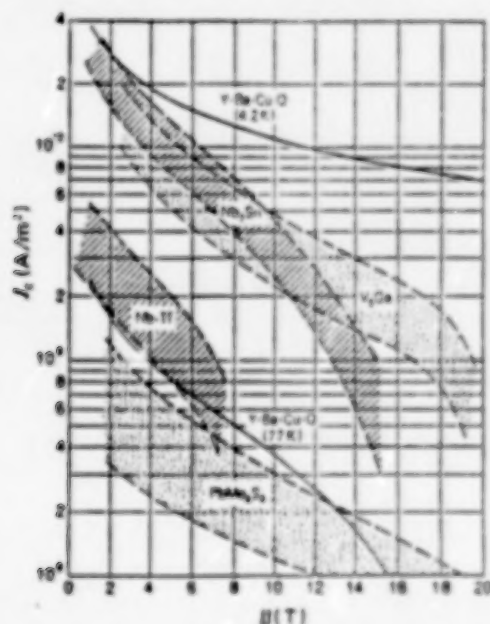


Figure 2. Critical Current Density of YBaCuO With Finely Grained or Oriented Structure and Those of Ordinary Superconductors

In sintered bodies and wire materials created by the powder method, there are insulating layers and voids and the crystals are oriented at random; thus, the above ideal case does not apply. The main factors determining the characteristics of these presently available materials comprise the interception of current paths by the above defects and the nonconformity in pinning the twinning plane randomly directed in the direction of the magnetic field. Here, let us first look, for simplicity's sake, not at the effects of the insulating layers but at the entire entity as a spherical (dodecahedral) grain assembly and use P_m as its superconductive proportion. Figure 3 shows the results of calculating critical current density derived by the theory of percolation in view of the fact of random orientation.⁶ Critical current density decreases as P_m approaches the critical percolation concentration of $P_c = 1/6$. The broken line represents simple average current density and gives the expected value of screened current in isolated grains. The measured intragrain current density has much the same value. In the future, improvement to the level of $P_m = 1$, namely, the level of intragrain screening current density, is likely to be possible. But this is far below the optimum level indicated in Figure 2, and for further improvement it is necessary either to reduce the grain size or to orient the twinning plane systematically. The fact that the present critical current density is smaller than its expected value is believed to be the effect of the insulating layer.

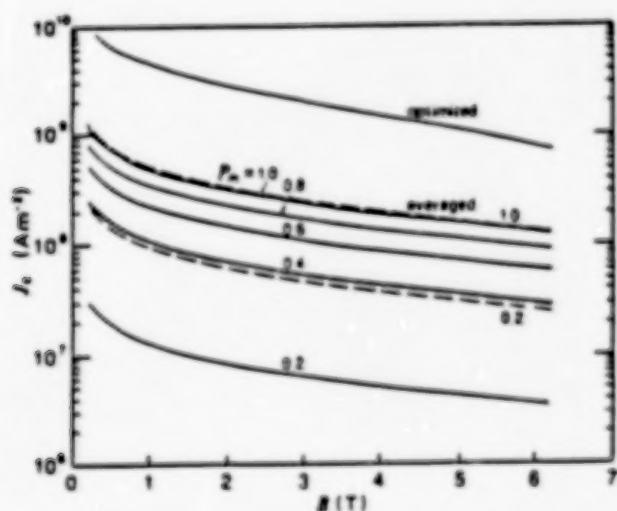


Figure 3. Critical Current Density of Sintered YBaCuO With Randomly Oriented Grains for Various Superconducting Fractions P_m . Broken lines are isolated intra-grain current density.

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